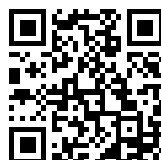

This is a reproduction of a library book that was digitized by Google as part of an ongoing effort to preserve the information in books and make it universally accessible.

GoogleTM books

<https://books.google.com>





THE
JOURNAL OF THE
ROYAL ANTHROPOLOGICAL INSTITUTE
OF GREAT BRITAIN AND IRELAND
OF
THE
JOURNAL OF THE
ROYAL ANTHROPOLOGICAL INSTITUTE
OF GREAT BRITAIN AND IRELAND

Volume 10, Part 1, 1900
Published by the Royal Anthropological Institute
of Great Britain and Ireland
21, BEDFORD SQUARE, LONDON, W.C.1
Price 10s. 6d. per volume
Single parts 2s. 6d.

Subscription prices for 1900
For the year 1900, 10s. 6d.
For the year 1901, 10s. 6d.
For the year 1902, 10s. 6d.
For the year 1903, 10s. 6d.
For the year 1904, 10s. 6d.
For the year 1905, 10s. 6d.
For the year 1906, 10s. 6d.
For the year 1907, 10s. 6d.
For the year 1908, 10s. 6d.
For the year 1909, 10s. 6d.
For the year 1910, 10s. 6d.

102

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

CONDUCTED BY

SIR OLIVER JOSEPH LODGE, D.Sc., LL.D., F.R.S.
SIR JOSEPH JOHN THOMSON, O.M., M.A., Sc.D., LL.D., F.R.S.
JOHN JOLY, M.A., D.Sc., F.R.S., F.G.S.
RICHARD TAUNTON FRANCIS

AND

WILLIAM FRANCIS, F.L.S.

"Nec aranearum sane textus ideo melior quia ex se fila gignunt, nec noster
vilior quia ex alienis libamus ut apes." JUST. LIPS. *Polit. lib. i. cap. 1. Not.*

VOL. XLV.—SIXTH SERIES.

JANUARY—JUNE 1923.

UNIVERSITY LIBRARY
PRINCETON, N. J.

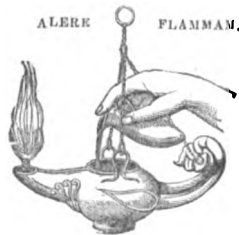
LONDON:

TAYLOR AND FRANCIS, RED LION COURT, FLEET STREET.
SOLD BY SMITH AND SON, GLASGOW;—HODGES, FIGGIS, AND CO., DUBLIN;—
AND VEUVE J. ROYVEAU, PARIS.

**"Meditationis est perscrutari occulta ; contemplationis est admirari
perspicua Admiratio generat quæstionem, quæstio investigationem,
investigatio inventionem."**—*Hugo de S. Victore*

— "Cur spirent venti, cur terra dehiscat,
Cur mare turgescat, pelago cur tantus amaro,
Cur caput obscura Phœbus ferrugine condant,
Quid toties diros cogat flagrare cometas,
Quid pariat nubes, veniant cur fulmina cælo,
Quo micet igne Iris, superos quis conciat orbes
Tam vario motu."

J. B. Pinelli ad Mazonium.



CONTENTS OF VOL. XLV.

(SIXTH SERIES).

NUMBER CCLXV.—JANUARY 1923.

	Page
Mr. R. H. Fowler on Dissociation-equilibria by the Method of Partitions	1
Dr. A. C. Crehore on the Process of Light Radiation from an Atom of a Gas leading to a Possible Interpretation of Planck's Quantum by means of Electrodynamics. IV.	34
Mr. Svein Rosseland on the Theory of Ionization by Swiftly Moving Electrified Particles and the Production of Characteristic X-Rays.	65
Mr. J. E. P. Wagstaff on Application of an Optical Manometer to the Measurement of the Viscosity of Gases	84
Mr. J. E. P. Wagstaff on the Shape of the Capillary Curve formed between a Flat Glass Plate and a Uniform Circular Cylinder, and the Accurate Determination of the Surface Tension of Liquids ..	88
Mr. Sasi Bhusan Mali on a Critical Review of Trouton's Law, and its Applicability at the Triple Point	94
The Research Staff of the General Electric Company, Ltd., London, on Cathode Disintegration.	98
Prof. C. V. Raman and Mr. K. R. Ramanathan on the Molecular Scattering of Light in Dense Vapours and Gases	113
Dr. H. J. S. Sand on the Anomaly of Strong Electrolytes with special Reference to the Theories of J. C. Ghosh	129
Prof. S. Boguslawski on the Problem of two Moving Charges in its connexion with the Atomic Theory.	145
Prof. Tch. Bialobjeski on the Theory of Metallic Conduction	161
Dr. R. A. Houstoun and Mr. E. Dow on the Evaluation of the Colours of the Spectrum in Terms of the Three Primary Colours.	169
Mr. T. Y. Thomas on the Equality of Tensors	177
Dr. F. H. Newman on Relative Visibility of Spectra when an Electric Discharge is passed through the Vapours of Alkali Amalgams (Plate I.)	181
Prof. Kōtarō Honda on the Theory of the Specific Heat of Liquids.	189
Mr. R. V. Southwell on Castigliano's Theorem of Least Work, and the Principle of St. Venant	193
Prof. C. V. Raman and Mr. K. R. Ramanathan on the Molecular Scattering of Light in Liquid Mixtures	213
Mr. R. N. Ghosh on a Qualitative Study of Infected Waves.	225
Prof. A. H. Gibson and Mr. F. Heywood on some Experiments on the Impact of Hydraulic Jets	229
Prof. H. M. Dadourian on a Simple Derivation of the Lorentz Transformations	238
Mr. Mituo Yamada on the Occlusion of Hydrogen in Palladium. (Plate II.)	241
Sir J. Larmor on the Nature and Amount of the Gravitational Deflexion of Light	243

Nov. 20. 23
E. H. M. Sec. Sci. - St.

80016th ser. 45
717
526323
(30. Jan. 1923)

NUMBER CCLXVI.—FEBRUARY.

	Page
Prof. H. Lamb on the Early Stages of a Submarine Explosion	257
Prof. G. N. Lewis on Physical Constants and Ultimate Rational Units	266
Mr. S. J. Gunningham on the Field of an Electron on Einstein's Theory	276
Dr. H. J. S. Sand on the Anomaly of Strong Electrolytes with special Reference to the Theories of J. C. Ghosh	281
Dr. F. H. Newman on the Visibility of Individual Spectra (Plate III.)	293
Prof. J. Kunz on a Derivation of Planck's Law of Radiation by means of the Adiabatic Hypothesis	300
Prof. J. Heyrovský on Electrolysis with a Dropping Mercury Cathode. Part I. Deposition of Alkali and Alkaline Earth Metals	303
Mr. R. N. Ghosh on Indian Drums	315
Mr. F. T. Peirce on Magnetic Valency and the Radiation Hypothesis.	317
Prof. A. W. Conway on the Orientation of the Bohr-Sommerfeld Orbits	324
Mr. C. H. Bickerdike on the Physical Interpretation of Relativity Mathematics	327
Mr. J. J. Manley on the Production of Coloured Flames for use with Spectrometers and Polarimeters	336
Prof. O. W. Richardson and Mr. R. Chaudhuri on the Effect of Gases in facilitating the Passage of Current from an Electron-Emitting Source in Crossed Electric and Magnetic Fields	337
Mr. T. L. R. Ayres on the Ionization by Collision of Hydrogen, Nitrogen, and Argon	353
Dr. D. Wrinch and Dr. H. Jeffreys on certain Fundamental Principles of Scientific Inquiry. (Second Paper.)	368
Mr. J. H. Smith on the Calculation of the Magneton Number of an Atom in Solution	375
Mr. C. W. van der Merwe on the Range of Alpha-Particles from Polonium in Various Gases. (Plate IV.)	379
Proceedings of the Geological Society	382-384

NUMBER CCLXVII.—MARCH.

Sir G. Greenhill on Precession of the Spinning Top (Plates V., VI., VII., & VIII.)	385
Dr. H. H. Poole on Tidal Stresses and Continental Displacements . .	399
Dr. E. V. Appleton and Mr. W. M. H. Greaves on the Solution of the Representative Differential Equation of the Triode Oscillator.	401
Mr. H. H. Platt on Restricted Movements of Molecules at very low pressures	414
Prof. J. R. Partington and Mr. W. G. Shilling on the Specific Heats of Nitrous and Nitric Oxides	416
Mr. P. Lasareff on the Question of the Number of Radiating Atoms of Various Dimension within Gaseous Hydrogen, studied from the point of view of Bohr's Atom Model	430
Mr. J. J. McHenry on Positive Rays in simple Gases	433
Prof. J. S. Townsend on Ionization by Collision	444
Mr. C. H. Bickerdike on Suggestions regarding an Alternative Theory	456

	Page
Prof. B. Davis and Mr. H. M. Terrill on a Determination of the Co-efficient of Reflexion of X-Rays for Calcite and Rock-salt	463
Prof. G. B. Deodhar on the Longitudinal Elasticity and Poisson's Ratio of India-rubber.....	471
Prof. W. M. Hicks on the Radiation and Ionization Potentials of the Rare Gases and on the Singlet and Enhanced Series of Argon ..	480
Mr. R. H. Fowler on Thermodynamics and Statistical Mechanics..	497
Mr. G. L. Addenbrooke on Electrical Properties of a Flint Glass of Density 6.01.....	516
Mr. C. H. Bosanquet on the Flow of Liquids into Capillary Tubes.	525
Messrs. F. Adcock and E. H. Wells on Temperature Measurement with the Einthoven Galvanometer. (Plates IX. & X.)	532
Prof. T. H. Havelock on Magnetic Rotary Dispersion in Gases	560
Prof. G. N. Watson on the Sum of Series of Coscants	577
Mr. H. G. Becker on a simple Form of Apparatus for observing the Rate of Reaction between Gases and Liquids, and its Use in determining the Rate of Solution of Oxygen by Water under Different Conditions of mixing	581
Dr. L. A. Welo on some Photoelectric Experiments on Platinum relating to the Influence of Gases.....	593
Prof. S. C. Kar on the Theory of Generalized Quanta and the Balmer Lines.....	610
Mr. A. F. Core on the Meaning of " <i>a</i> " and " <i>b</i> " in the Equation of State	622
Prof. C. V. Raman and Mr. K. Seshagiri Rao on the Molecular Scattering and Extinction of Light in Liquids and the Determination of the Avogadro Constant	625
Intelligence and Miscellaneous Articles:—	
On the Viscosity of Gases in a Transverse Electric Field, by H. Sirk.....	640

NUMBER CCLXVIII.—APRIL.

Prof. W. G. Duffield on the Reaction consequent upon the Evaporation of a Liquid and upon the Emission of Vapours from Small Orifices.—Part I. Argument. Part II. Appendix	641.
Mr. S. Lees on the Whirling of an Overhung Eccentrically Loaded Shaft.....	689
Prof. W. McF. Orr: Note on Mr. Lees' Paper on the Whirling of an Overhung Shaft	708
Dr. F. C. Toy on the Theory of the Characteristic Curve of a Photographic Emulsion.—Part II.....	715
Mr. J. T. Combridge on the Gravitational Field of a Particle on Einstein's Theory	726
Dr. C. Jordan on the Inversion of Bernoulli's Theorem	732
Mr. J. R. Clarke on the Fluorescence and Coloration of Glass produced by β -rays.	735
Prof. C. G. Barkla and Miss R. R. C. Sale on X-Ray Scattering and on J Radiations.....	737
Prof. K. T. Compton on some Properties of Resonance Radiation and Excited Atoms.....	750
Messrs. L. T. Jones and W. C. Pomeroy on Testing the Expressions for the Longitudinal and Transverse Masses of the Electron	760

	Page
Prof. G. A. Schott: Does an accelerated Electron necessarily radiate Energy on the Classical Theory?	769
Mr. F. J. W. Whipple on the Disturbance of the Uniform Temperature of the Stratosphere by the Vertical Displacement associated with Horizontal Motion governed by the "Geostrophic Law."	778
Mr. F. B. Pidduck on the Calculation of High-Frequency Inductances.	783
Dr. A. C. Davies on Critical Electron Energies in Helium, and the Extreme Ultra-Violet Spectrum	786
Proceedings of the Geological Society:—	
Dr. H. A. Baker on Geological Investigations in the Falkland Islands	798
Intelligence and Miscellaneous Articles:—	
On the Failure of the Reciprocity Law in Photography, by R. A. Mallet	800
Precession of the Spinning Top, by Sir G. Greenhill	800

NUMBER CCLXIX.—MAY.

Dr. J. W. Nicholson on the Quantum Theory and Isotopes	801
Dr. D. M. Wrinch on some Approximations to Hypergeometric Functions	818
Prof. A. L. Narayan and Mr. D. Gunnayya on Emission and Absorption of Halogens in the Visible and Ultra-violet Regions. (Plate XI.)	827
Prof. A. L. Narayan and Mr. D. Gunnayya on Absorption of Potassium Vapour. (Plate XII.)	831
Prof. W. E. Adeney, Dr. A. G. G. Leonard, and A. Richardson on the Aeration of Quiescent Columns of Distilled Water and of Solutions of Sodium Chloride	835
Mr. H. E. H. Wrinch and Dr. D. Wrinch: Tables of the Bessel Function $J_n(x)$	846
Dr. C. P. Smyth on the Calculation of the Electric Moment of the Molecule of a Substance	849
Mr. E. W. B. Gill on the Emission of Secondary Electrons from Nickel	864
Dr. E. V. Appleton and Mr. A. G. D. West on Ionic Oscillations in the Striated Glow Discharge	879
Miss Ida Woodward on an Investigation of the Structure of the Halogen Salts based on their Compressibility	882
Dr. J. H. J. Poole on the Variation of the Photo-electric Activity of a Potassium ferro-cyanide solution with the Concentration of the solution.	895
Mr. H. G. Green on the Velocity of Sound in Liquids contained in Circular Cylinders with slightly Elastic Walls	907
Mr. A. G. Shenstone on the Effect of Current on the Photo-electric Sensitivity of Metals	918
Mr. R. C. Richards on the Resistance of a Hot Wire in an Alternating Air Current	926
Dr. F. W. Aston on the Mass-spectra of Chemical Elements.—Part IV. (Plate XIII.)	934
Dr. J. S. G. Thomas on the Hot-Wire Inclinator: its Sensitivity in Air and in Carbon Dioxide.	945
Mr. J. Ewles on Cathodo-Luminescence and its Relation to States of Molecular Aggregation.	957

Mr. J. D. Morgan on some Observations on the Ignition of Combustible Gases by Electric Sparks	968
Mr. E. G. Richardson on the Theory of the Trevelyan Rocker....	976
Mr. P. L. Kapitza on the Theory of δ -Radiation	989
Mr. P. Franklin on Tensors of given Types in Riemann Space....	998
Mr. R. A. Watson Watt on Directional Observations of Atmospherics—1916–1920.....	1010
Mr. F. F. P. Bisacre on the Calculation of the Skin Effect in Electrical Conductors	1026
Prof. D. M. Bose and Mr. S. K. Ghosh on Photographing the Ionization Tracks of the Rest Atoms of Radioactive Elements. (Plate XIV.)	1050
Mr. H. Carrington on the Elastic Constants of Spruce	1055
Prof. W. Peddie on the Physics of Colour Vision	1058
Dr. L. Silberstein on Quantum Theory of Photographic Exposure. (Third Paper.)	1062
Prof. J. S. Townsend on Ionization by Collision in Helium	1071
Dr. R. T. Beatty on the Distribution of Energy in the Lines of the Balmer Series of Hydrogen.....	1080
Mr. H. O. Newbould on the Stark Effect for Strong Electric Field.	1081
Mr. H. O. Newbould on the Spectrum of the Semi-circular Helium Model	1085
Mr. T. Iredale on Adsorption from the Gas Phase at a Liquid-Gas Interface.—Part I.	1088
Notices respecting New Books:—	
Mr. E. H. Neville's Prolegomena to Analytical Geometry in Anisotropic Euclidean Space of Three Dimensions	1100
Capt. C. S. Wright's British (Terra Nova) Antarctic Expedition (1910–1913)	1101
Tables Annuelles Internationales de Constantes et Données Numériques de Chimie, de Physique et de Technologie....	1102
Dr. Kaye's X Rays	1102
Prof. A. N. Whitehead's The Principle of Relativity with applications to Physical Science	1103
Intelligence and Miscellaneous Articles:—	
The Reaction consequent upon the Evaporation of a Liquid and upon the Emission of Vapours from Small Orifices	1104

NUMBER CCLXX.—JUNE.

Prof. T. M. Lowry on the Electronic Theory of Valency.—I. Intramolecular Ionization.....	1105
Prof. F. A. Lindemann on the Theory of the Specific Heat of Liquids	1119
Prof. A. H. Compton on the Total Reflexion of X-Rays	1121
Dr. H. P. Waran on Luminous Pulsations in the Glow of Phosphorus.	1132
Prof. W. G. Duffield on the Mechanism of the Electric Arc	1139
The Research Staff of the General Electric Co., Ltd., London, on a Theory of the Abnormal Cathode Fall	1149
Dr. G. Green on an Extended Application of the Principle of Stationary Phase in Wave-Motion Problems	1156
Prof. J. Joly on the Movements of the Earth's Surface Crust	1167

Notices respecting New Books :—

Messrs. P. Hass and T. G. Hill's <i>An Introduction to the Chemistry of Plant Products. Volume 2. Metabolic Processes.</i>	1189
Prof. A. S. Eddington's <i>The Mathematical Theory of Relativity.</i>	1189
Prof. H. F. Baker's <i>Principles of Geometry</i>	1190
Prof. J. F. Thorpe and Dr. C. K. Ingold's <i>Synthetic Colouring Matters : Vat Colours</i>	1191

Intelligence and Miscellaneous Articles :—

On Electric Fields due to the Motion of Constant Electromagnetic Systems, by W. F. G. Swann	1191
---	------

Index	1193
-------------	------

P L A T E S.

- I. Illustrative of Dr. F. H. Newman's Paper on Relative Visibility of Spectra when an Electric Discharge is passed through the Vapours of Alkali Amalgams.
- II. Illustrative of Mr. Mituo Yamada's Paper on the Occlusion of Hydrogen in Palladium.
- III. Illustrative of Dr. F. H. Newman's Paper on the Visibility of Individual Spectra.
- IV. Illustrative of Mr. C. W. van der Merwe's Paper on the Range of Alpha-Particles from Polonium in Various Gases.
- V., VI., VII., & VIII. Illustrative of Sir G. Greenhill's Paper on Precession of the Spinning Top.
- IX. & X. Illustrative of Messrs. F. Adcock and E. H. Wells's Paper on Temperature Measurement with the Einthoven Galvanometer.
- XI. Illustrative of Prof. A. L. Narayan and Mr. D. Gunnayya's Paper on Emission and Absorption of Halogens in the Visible and Ultra-violet Regions.
- XII. Illustrative of Prof. A. L. Narayan and Mr. D. Gunnayya's Paper on Absorption of Potassium Vapour.
- XIII. Illustrative of Dr. F. W. Aston's Paper on the Mass-spectra of Chemical Elements.
- XIV. Illustrative of Prof. D. M. Bose and Mr. S. K. Ghosh's Paper on Photographing the Ionization Tracks of the Rest Atoms of Radioactive Elements.

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

JANUARY 1923.

I. *Dissociation-equilibria by the Method of Partitions.* By
R. H. FOWLER, M.A., *Fellow and Lecturer in Trinity
College, Cambridge* *.

§ 1. *INTRODUCTION and Summary of the paper.*—In two previous papers† Mr. Darwin and I have treated the usual problems of the partition of energy in statistical mechanics by a more powerful method than has hitherto been used. This method allowed us to obtain all the usual formulæ of statistical equilibrium by the direct calculation of averages, avoiding entirely the need for any appeal to entropy. In the second paper we examined the whole position of entropy in statistical theory, and concluded that, though a proper logical account of it is possible, such an account must be somewhat recondite, and that the whole idea is really unnecessary in statistical work. Practically speaking, before entropy can be properly introduced the whole statistical problem for which it might be helpful has been otherwise solved.

These two papers apply only to assemblies of systems in which the various systems retain an individual existence throughout—that is to say, all cases of dissociation were

* Communicated by the Author.

† *Phil. Mag.* Sept. and Nov. 1922: "On the Partition of Energy," Parts I. and II. These two papers will be referred to as first and second paper respectively. As I need scarcely say, I am, in this paper, deeply indebted to Mr. Darwin, who must not, however, be held responsible for its imperfections.

Phil. Mag. S. 6. Vol. 45. No. 265. Jan. 1923.

B

specifically excluded. The method can, however, be extended, with some loss of elegance, to assemblies in which dissociation occurs. It is still, however, simple and satisfactory, and in addition leads to what I believe to be extensions of known results. The equilibrium of such assemblies treated by purely statistical methods forms the subject of this paper which is Part III. of the series.

The problems of dissociation have recently been treated by Ehrenfest and Trkal* from the statistical standpoint in a most interesting paper. They maintain the position that the study of chemical constants, thermodynamic probability, and absolute entropy, which is left in considerable obscurity by earlier writers†, can only be logically approached by a statistical study of the dissociation-equilibria of molecules and atoms. However, they only discuss the dissociation problem on semi-classical lines: they assume, that is, that all degrees of freedom are either "fully excited" so that the classical theory is adequate, or "completely unexcited" in which case they may be ignored. This restriction can be removed so as to treat the statistical problem of dissociation quite generally—generally that is to say from the mathematical point of view. The difficulties which are met with and restrict the range of the results are no longer mathematical but apparently physical and inherent in the problem.

In our second paper Mr. Darwin and I have already discussed in some detail the same questions of thermodynamic probability and absolute entropy, but of course without including cases of dissociation. With the position maintained by Ehrenfest and Trkal we are in complete agreement, and with the help of the results here obtained this discussion can be carried further.

It is convenient to outline here the scope of the present paper. In § 2 I summarize the results of our previous papers so far as they are required here. In §§ 3-6 I introduce the study of the dissociation problem by the discussion in detail of the simplest case, the reaction $X_2 \rightleftharpoons 2X$. This suffices to bring out all the salient features of the method and the extensions to previous results which are possible by its aid. In § 7 the results are applied in

* Ehrenfest and Trkal, Proc. Sect. Sciences Amsterdam, vol. xxiii. p. 162 (1920).

† M. Planck, *Wärmestrahlung*, 3rd ed. §§ 127, *sqq.*; O. Sackur, *Ann. der Physik*, vol. xxxvi. p. 958 (1911), vol. xl. p. 67 (1913); H. Tetrode, *Ann. der Physik*, vol. xxxviii. p. 434 (1912); etc.

general terms to Saha's* theory of the ionization in stellar atmospheres. This is perhaps the most interesting application of the theory of dissociation-equilibria. Saha's fundamental formula is based on the whole apparatus of chemical constants and Nernst's Heat Theorem. In view of its importance, and the somewhat unsatisfactory nature of its basis, it is of interest to present this formula in its proper form as a theorem in statistical mechanics. In so doing, one can obtain a clearer insight into the exact assumptions on which it is based. One is led to the conclusion that the usual formula is not necessarily correct—a further term should be included whose effect may be of great importance. This extra term unfortunately may make Saha's formula less definite, and the detailed application of the new formula must be postponed for further investigation. The discussion of the temperature ionization of a gas introduces us to a fundamental difficulty in the statistics of the Hydrogen (or any other) atom†. This is considered in detail in § 8. In § 9 the results of §§ 3–6 are extended to the general dissociation problem.

In § 10 I consider by the same method the general vapour-pressure equation, which is also discussed by Ehrenfest and Trkal‡. This leads in § 11 to general formulæ for the chemical constants, which show up their dependence on the weights of the lowest permitted quantum states of the molecules. In particular, it is now possible to discuss adequately the chemical constant of H_2 in the region in which it behaves effectively like a monatomic gas. The agreement of its chemical constant with both theory and experiment for genuine monatomic gases is shown to provide important additional evidence as to the weights to be assigned to the first two quantum states of the rotational motion. In particular, it confirms the absence of the state of no rotation demanded by the evidence of band-spectra in general and by the curve of its own specific heats. Finally, the constants in the dissociation equations are expressed in terms of the chemical constants introduced into the vapour-pressure equations. The whole of these relations can be presented, and are

* M. N. Saha, *Phil. Mag.* vol. xl. pp. 472, 809 (1920); *Proc. Roy. Soc.* vol. xcix. A. p. 135 (1921). For general expositions, see E. A. Milne, *The Observatory*, vol. xlv. p. 261 (Sept. 1921); H. N. Russell, *Astroph. Journ.* vol. lv. p. 119 (1922).

† K. F. Herzfeld, *Ann. der Physik*, vol. li. p. 262 (1916).

‡ *Loc. cit.*, additional notes No. III.

here presented, as theorems in pure statistical mechanics based on the general principles of the quantum theory.

It is natural to follow up these theorems with the extended discussion of entropy referred to above, and in particular of Nernst's heat theorem and its relationship to the weight of the lowest quantum state of the systems concerned. This has been already pointed out in a preliminary way*, but with the additional theoretical material now available the connexion can be brought out more clearly. This discussion must, however, form the subject of another paper—it is unduly long for inclusion here.

§ 2. *Summary of previous results on Partitions.*—In the previous papers by Mr. Darwin and myself we have expounded a method of evaluating the partition of energy for various types of assembly. The essential point of our method is the calculation of average values by means of integrals whose integrands are simply expressed in terms of “partition functions.” There is a certain partition function for each type of system in the assembly—quantized or classical, the latter being obtained by a limiting process. By such means the tiresome combinatory expressions are very easily handled, and the integrals which give the average values and the fluctuations about those average values can be simply evaluated by the “method of steepest descents.”

The partition function—which in a different notation is the “Zustandsumme” of Planck—is constructed as follows. The physically possible states of the system are enumerated. These form a (generally infinite) series of discrete states for a quantized system; for the systems of classical mechanics the available phase-space must be divided into cells, all of whose dimensions must ultimately be made to tend to zero. To each state attaches a weight. The weight of any cell of a system obeying Hamiltonian equations is proportional to its extension. The relative weights of the cells of a quantized system are (at any rate in simple cases) determinable by the use of Bohr's Correspondence Principle and Ehrenfest's Adiabatic Hypothesis. No further *a priori* principle appears to be required. All weights are then definitely fixed by the convention † that

* Second paper, § 8.

† This convention is the simplest and most convenient that can be made (first paper, § 2), though it differs from that of Ehrenfest and Trkal (*loc. cit.*) by a constant factor. But in no case can a constant factor in *all* the weights affect any physical result.

any one state of a simple quantized system shall have unit weight. It should be remembered, however*, that the only essential condition attaching to the weights is precisely analogous to that attaching to entropy in classical thermodynamics—a definite ratio is required (and must be assignable) between the weights of two states of a system (or systems) which can pass from one to the other, but as long as the two states (or systems) are mutually non-convertible their weights are non-comparable and may have any ratio whatever. In the dissociation problem a quantized system (a molecule) can turn into two or more classical systems (free atoms), and so the complete specification of relative weights outlined above is relevant and must be retained. It has been used for simplicity throughout these papers. It here, for the first time, plays an integral part in the formulæ.

Associated with any state or cell there is a definite energy depending on the cell and (possibly) on certain parameters defining the external fields of force. Then, if p_r is the weight and ϵ_r the energy in the r th state or cell for any particular system, the partition function is defined in terms of a certain additional parameter $\mathfrak{S}$ by the equation

$$f(\mathfrak{S}) = \sum_r p_r \mathfrak{S}^{\epsilon_r}, \quad \dots \dots \dots (2.1)$$

summed over all states or cells. It is a function of $\mathfrak{S}$, x_1 , x_2 , ... For classical systems the sum must be replaced by its limit when all the dimensions of all the cells tend to zero, that is by an integral; but this limit can be used in all formulæ without restriction†, exactly as if it were still of the form (2.1).

We recall certain examples of partition functions.

(i.) Planck's line vibrator :

$$f(\mathfrak{S}) = \frac{1}{1 - \mathfrak{S}^\epsilon}, \quad (\epsilon = h\nu). \quad \dots \dots \dots (2.21)$$

(ii.) The rotations of a diatomic molecule of transverse moment of inertia J ‡ :

$$f(\mathfrak{S}) = 1 + 3\mathfrak{S}^\epsilon + 5\mathfrak{S}^{4\epsilon} + 7\mathfrak{S}^{9\epsilon} + \dots, \quad \left(\epsilon = \frac{h^2}{8\pi^2 J} \right). \quad (2.22)$$

* Second paper, § 8.

† First paper, § 12. For further details, see a forthcoming paper in Proc. Camb. Phil. Soc. (1922).

‡ The weight $2n+1$ assigned to the n th quantum state must on general principles be correct if none of the apparently possible states are barred. This was pointed out in our first paper, § 11. It is so to speak the maximum value of the weight. But there is a good

(iii.) Free monatomic molecules of mass m in a volume V :

$$f(\mathfrak{S}) = \frac{(2\pi m)^{3/2} V}{h^3 (\log 1/\mathfrak{S})^{3/2}} \dots \dots \dots (2\cdot23)$$

If any system is capable of two or more types of motion which are independent of one another—for example, the motions of translation and rotation of a di- or polyatomic molecule—the partition functions for the two types can be calculated separately and their product is the partition function for the whole motion of the system.

With the help of these partition functions we construct an integral for C , the total number of *weighted complexions**, which enumerates all possible states of any assembly of systems whose total energy is E . If there are M_A systems of type A with partition function f_A etc., then

$$C = \frac{1}{2\pi i} \int_{\gamma} \frac{dz}{z^{E+1}} [f_A(z)]^{M_A} [f_B(z)]^{M_B} \dots \dots \dots (2\cdot3)$$

the contour γ is any circle round the origin of radius less than unity. Similar integrals can at once be obtained for $C\bar{E}_A$, where $\bar{E}_A$ is the average energy held by the systems A , or $C\bar{a}_r$, where $\bar{a}_r$ is the average number of systems A in their r th quantum state.

These integrals are easily evaluated approximately (E and the M 's all large). It is found that there is a *unique* real number $\mathfrak{S}$, $0 < \mathfrak{S} < 1$, determined by the equation

$$E = \sum_A M_A \mathfrak{S} \frac{d}{d\mathfrak{S}} \log f_A, \dots \dots \dots (2\cdot31)$$

and that if the contour γ passes through $\mathfrak{S}$ the whole value of the integral is contributed by a small part of the contour near $z = \mathfrak{S}$. We thus find

$$\bar{E}_A = M_A \mathfrak{S} \frac{d}{d\mathfrak{S}} \log f_A, \dots \dots \dots (2\cdot32)$$

$$\bar{a}_r = M_A \rho_{A,r} \mathfrak{S}^{E_{A,r}} / f_A \dots \dots \dots (2\cdot33)$$

deal of evidence, some of which we must consider in later sections, that not all these states can be permissible. The first term may be and probably is missing, and the later weights may be $2n$ instead of $2n+1$. See Reiche, *Ann. der Physik*, vol. lviii. p. 657 (1919). Reiche considers also n and $n+1$ as possible values; but, as we shall see in §11, these cannot be allowed if full agreement in the limit with classical mechanics is to be maintained. Whatever the precise form of $f(\mathfrak{S})$ its treatment here is unaffected.

* We use complexions in an extended sense to cover the case in which we have already proceeded to the limit for classical systems. For the legitimacy of this, see reference in last footnote.

We then identify $\mathfrak{S}$ with the temperature on an empirical scale and prove that in all cases it must be related to the absolute temperature T by the equation

$$\mathfrak{S} = e^{-1/kT}, \quad \dots \quad (2.4)$$

where k is Boltzmann's constant.

The average values above are shown to be normal properties of the assembly by evaluating their fluctuations $(E_A - \overline{E_A})^2$ etc., and showing that $(E_A - \overline{E_A})^2$ is of the same order as $\overline{E_A}$, therefore negligible compared with $(\overline{E_A})^2$.

§3. The Dissociation-equilibrium of the reaction $X_2 \rightleftharpoons 2X$.

To simplify the formulæ and exhibit in the clearest way the important points in the argument, I have thought it best to begin by discussing the simplest case, in which only one kind of atom is present and only one reaction can occur. In any such problem, as Ehrenfest and Trkal point out, it is not really allowable to treat the internal vibrations of the diatomic molecule along its axis of symmetry as completely unexcited*. This degree of freedom must be allowed its proper share of energy, which may be appreciable if there is appreciable dissociation. We must also of course include the kinetic energy of translation of both atoms and molecules and the rotations of the latter about any transverse axis. Axial rotations of the molecules and all rotations of the atoms can be ignored as completely unexcited. There is no difficulty in formally including them if required.

Let us suppose that the partition function for the combined transverse rotations and vibrations of the molecule X_2 is, in general terms, $b(z)$ †. It is not properly possible to divide $b(z)$ into factors for the rotations and vibrations separately, for the two motions are not independent. We shall discuss shortly the details of the specification of $b(z)$ in §4. Further, let $h_1(z)$ be the partition function for the kinetic energy of translation of the atoms (mass m) and $h_2(z)$ for the molecules (mass $2m$); $h_1(z)$ and $h_2(z)$ are given by (2.23).

The number of weighted complexions c for an assembly of M atoms X and N molecules X_2 in a volume V with energy F available for distribution is by (2.3),

$$c = \frac{1}{2\pi i} \int_{\gamma} \frac{dz}{z^{F+1}} [h_1(z)]^M [h_2(z)b(z)]^N. \quad \dots \quad (3.1)$$

* It is by including this and similar quantized motions that the results of these authors are extended and completed in this paper.

† Ultimately $b(z)$ is determined by and determines the band spectrum of the molecule.

This, however, is no longer the total number of complexions of which the assembly is capable ; for M and N can change. We must take account of all possible values of M and N and all possible ways in which the assembly with given M and N can be constructed out of a total of X atoms. This part of the problem is completely discussed by Ehrenfest and Trkal*. They show that the total number of essentially different ways in which an assembly of M atoms and N molecules can be built up out of a total of X atoms is

$$\frac{X!}{M! N! \sigma^N}, \quad \dots \quad (3.2)$$

where

$$X = M + 2N, \quad \dots \quad (3.21)$$

and σ is the symmetry number † of the molecule, which in this case is 2. We shall retain the symbol σ in the calculations.

Since there are $X!/(M! N! \sigma^N)$ examples of the assembly with M atoms and N molecules each represented by c weighted complexions, the full number of complexions representing the assembly in this statistical state is

$$\frac{X! c}{M! N! \sigma^N}, \quad \dots \quad (3.3)$$

The total C of all complexions representing the assembly is obtained by summing (3.3) over all values of M and N subject to (3.21) and the condition of constant total energy. The energy F available for distribution among the partition functions when there are M atoms and N molecules depends on M and N. If χ is the heat of dissociation per molecule, or the work required to separate one molecule into two independent atoms, we can express F in terms of χ . For the sake of preciseness, let us take the state of zero energy of the assembly as that in which the molecules are all dissociated

* *Loc. cit.* §4, equation (18). It is in the treatment of what Ehrenfest and Trkal call the “ μ -weight” that our discussions diverge, allowing of increased generality here.

† The symmetry number of a molecule (Ehrenfest and Trkal, *loc. cit.* p. 163) is the number of different orientations which it can take up without altering the distribution in space of any type of atom. The expression $X!/(M! N!)$ gives the number of arrangements of the X atoms to form M atoms and N molecules, and arrangements in which the molecules X_1X_2 and X_2X_1 occur are counted as different. But owing to the rotational freedom of the molecule these arrangements are not really distinct, and the above expression must therefore be divided by 2^N . For a molecule with tetrahedral symmetry such as C11, $\sigma=12$, and so on.

and the resulting X atoms all at rest. The assembly can then have negative energies, but this is of no importance. Let us take the state of zero energy of a molecule to be its state when it has no rotation* or velocity of translation and no internal energy of vibration. It is then in its lowest quantum state, and χ must be taken to be the work required to separate such a molecule into two independent atoms at rest. In the ordinary process in which atoms combine to form molecules with evolution of heat, $\chi > 0$. Observe that χ is an absolute constant. The fact that not all molecules are in their lowest quantum state does not alter χ . This fact is taken full account of by the partition function $b(z)$. If E is the total energy of the assembly (relative to our conventional zero), then

$$F = E + N\chi, \quad \dots \quad (3.4)$$

and therefore

$$\begin{aligned} C &= \sum_{M+2N=X} \frac{X!}{M! N! \sigma^N} \frac{1}{2\pi i} \int_{\gamma} \frac{dz}{z^{E+1}} [h_1(z)]^M \left[\frac{h_2(z)b(z)}{z^X} \right]^N \\ &= \frac{1}{2\pi i} \int_{\gamma} \frac{dz}{z^{E+1}} [h_1(z)]^X \sum_N \frac{X! \beta^N}{N! (X-2N)!}, \quad \dots \quad (3.5) \end{aligned}$$

where

$$\beta = \frac{h_2(z)b(z)}{\sigma z^X \{h_1(z)\}^2}, \quad \dots \quad (3.51)$$

Exactly similar integrals can be obtained at once for $C\bar{N}$ etc., which give us the degree of dissociation and its fluctuations if required. Thus by (3.3),

$$C\bar{N} = \frac{1}{2\pi i} \int_{\gamma} \frac{dz}{z^{E+1}} [h_1(z)]^X \sum_N \frac{NX! \beta^N}{N! (X-2N)!}. \quad (3.52)$$

We show how to evaluate these and similar integrals in § 5. We give in advance the principal result, which is that

$$\frac{\bar{N}}{(X-2\bar{N})^2} = \frac{\bar{N}}{(\bar{M})^2} = \beta(\vartheta) = \frac{h_2(\vartheta)b(\vartheta)}{\sigma \vartheta^X \{h_1(\vartheta)\}^2}, \quad \dots \quad (3.6)$$

Equation (3.6) gives the dissociation-equilibrium, "the reaction-isobar," as a function of the temperature. Its physical form is discussed shortly in the next section.

* The arguments are easily adapted to include the case in which this state is not permitted; see § 4.

§ 4. *The form of the Reaction-isobar for $X_2 \rightleftharpoons 2X$.*— If we insert known values for the functions $h(\mathfrak{S})$ and for σ in (3.6) we get

$$\begin{aligned} \frac{VN}{(M)^2} &= \frac{h^3}{2(\pi m)^{3/2}} \frac{(\log 1/\mathfrak{S})^{3/2}}{\mathfrak{S}x} b(\mathfrak{S}) \\ &= \frac{h^3}{2(\pi km)^{3/2}} T^{-3/2} e^{x/kT} B(T). \quad (4.1) \end{aligned}$$

Expressed in terms of molecular densities $\nu_1 = \bar{M}/V$, $\nu_2 = \bar{N}/V$, we have

$$\frac{\nu_2}{\nu_1^2} = \frac{h^3}{2(\pi km)^{3/2}} T^{-3/2} e^{x/kT} B(T). \quad (4.11)$$

As we have assumed that the individual gases (of molecules and of atoms) are perfect, we can transform to partial pressures p_1, p_2 by $p_1 = \nu_1 kT$, $p_2 = \nu_2 kT$. If, further, x is the fraction of molecules dissociated and P the total pressure, then

$$\begin{aligned} p_1 &= \frac{2xP}{1+x}, \quad p_2 = \frac{(1-x)P}{1+x}, \\ \frac{1-x^2}{4x^2P} &= \frac{h^3}{2(\pi m)^{3/2} k^{5/2}} T^{-5/2} e^{x/kT} B(T). \quad (4.12) \end{aligned}$$

The essentially new feature in these equations is the occurrence in its proper place of the factor $b(\mathfrak{S})$ or $B(T)$.

The term $b(\mathfrak{S})$ is the partition function for the rotational and vibrational energy of the molecules. As we have already said, these cannot strictly be separated. But as a first approximation these motions are independent and the separation can be made, as is shown by the evidence of band spectra. Thus

$$b(\mathfrak{S}) = r(\mathfrak{S}) v(\mathfrak{S}).$$

We suppose that J the moment of inertia is roughly constant to the order of accuracy with which we can discuss $b(\mathfrak{S})$; then $r(\mathfrak{S})$ is given by (2.22) unless the rotationless molecule is impossible*, in which case the term 1 must be omitted. When $\mathfrak{S} \rightarrow 0$ ($T \rightarrow 0$),

$$r(\mathfrak{S}) \rightarrow 1, \quad r(\mathfrak{S}) \sim p_1 e^{-\epsilon/kT}, \quad (p_1 = 2 \text{ or } 3), \quad (4.2)$$

* There is strong evidence from band spectra (Sommerfeld, *Atombau und Spectrallinien*, ed. 3, chap. 7) and specific heats (Reiche, *loc. cit.*) that this state is impossible.

according as the term 1 is or is not to be retained. When $\mathfrak{S} \rightarrow 1$ ($T \rightarrow \infty$), in either case *

$$v(\mathfrak{S}) \sim \frac{8\pi^2 J k T}{h^2}, \quad \dots \quad (4.21)$$

giving the usual classical contribution R to the molecular specific heats.

For the vibrational term $v(\mathfrak{S})$ one may suppose for a similar rough approximation that the vibrations are like those of Planck's line vibrator, but that as an energy χ will dissociate the molecule no more than p states are possible in which the molecule remains a molecule. Then

$$v(\mathfrak{S}) = 1 + \mathfrak{S}^v + \dots + \mathfrak{S}^{(p-1)v} = \frac{1 - \mathfrak{S}^{pv}}{1 - \mathfrak{S}^v}. \quad \dots \quad (4.3)$$

It is somewhat less arbitrary to suppose that we may take

$$v(\mathfrak{S}) = 1 + \mathfrak{S}^{v_1} + \dots + \mathfrak{S}^{v_{p-1}}, \quad (0 < v_1 < v_2 < \dots < v_{p-1} < \chi); \quad \dots \quad (4.31)$$

the weights are necessarily all unity. When $\mathfrak{S} \rightarrow 0$ ($T \rightarrow 0$), $v(\mathfrak{S}) \rightarrow 1$. When $\mathfrak{S} \rightarrow 1$ ($T \rightarrow \infty$), $v(\mathfrak{S}) \rightarrow p$.

With reference to large values of T , it should, however, be observed that if χ and therefore pv are fairly large compared with v , there will be a considerable interval of values of $\mathfrak{S}$ or T in which $\mathfrak{S}^v$ is nearly 1 while $\mathfrak{S}^{pv}$ is still small, and in fact negligible compared with 1. Thus, for such values of T that $\dagger pv \gg T \gg v$,

$$v(\mathfrak{S}) = \frac{1}{1 - \mathfrak{S}^v} = \frac{kT}{v}, \quad \frac{\mathfrak{S} v'(\mathfrak{S})}{v(\mathfrak{S})} = \frac{v}{\mathfrak{S}^{-v} - 1} = kT,$$

approximately. We can of course write $v = h\nu_0$, where ν_0 is the fundamental frequency of the band spectrum. Thus at such temperatures the specific heat at constant volume of our molecular gas may reach effectively the value $\frac{7}{2}R$ or 6.96 calories per gram-molecule $\ddagger$ in spite of the limitation to p states. A similar result must hold for the $v(\mathfrak{S})$ given by (4.31) if the v_p do not differ much from multiples of v .

* By a theorem of Cesaro's: Bromwich, 'Infinite Series,' p. 132. Equation (4.21) holds for the weights $2n$ or $2n+1$, but not of course for the weight n .

$\dagger$ The notation $x \gg y$ is coming into increasing use in Mathematical Physics to denote " x is large compared with y ." It is a convenient and significant symbolism, which is adopted in this paper.

$\ddagger$ For example, C_v for the molecule I_2 is stated to reach this value at about 600° C. Stern, *Ann. der Physik*, vol. xlv. p. 512 (1914).

The evidence of band spectra shows that in general the ν -terms are considerably greater than the rotation ϵ -terms ($\epsilon = \frac{h^2}{8\pi^2 J}$); so that the rotations can be regarded as fully excited, while the vibrations are still practically unexcited. In such a case the formula for the reaction-isobar takes successively the approximate forms

$$\frac{1-x^2}{4x^2 P} = \frac{h^3}{2(\pi m)^{3/2} k^{5/2}} T^{-5/2} e^{\chi/kT}, \quad (kT \ll \epsilon), \quad . \quad . \quad . \quad (4.41)$$

$$\text{or} \quad \frac{\rho h^3}{2(\pi m)^{3/2} k^{5/2}} T^{-5/2} e^{(\chi-\epsilon)/kT}, \quad (\rho_1 = 2 \text{ or } 3), \quad . \quad (4.42)$$

$$= \frac{4\pi^{1/2} h J}{(km)^{3/2}} T^{-3/2} e^{\chi/kT}, \quad (\epsilon \ll kT \leq \chi, \nu), \quad . \quad . \quad (4.43)$$

$$= \frac{4\pi^{1/2} J}{\nu_0 k^{1/2} m^{3/2}} T^{-1/2} e^{\chi/kT}, \quad (\nu \leq kT \leq \chi), \quad . \quad . \quad (4.44)$$

$$= \frac{4\pi^{1/2} h J}{(km)^{3/2}} T^{-3/2} e^{\chi/kT}, \quad (\chi \leq kT). \quad . \quad . \quad . \quad (4.45)$$

Equation (4.42) refers to the case in which no rotation is impossible; the molecule of lowest quantum grade has no longer no energy, but energy ϵ . Since χ retains its old meaning, $\chi - \epsilon$ is now the heat of dissociation per molecule. Thus (4.41) and (4.42) essentially differ only in the constant factor ρ_1 , which arises from the different weights which must be assigned in these cases to the lowest quantum state. Equation (4.43) corresponds to the conditions considered by Ehrenfest and Trkal, and agrees with their result, but only if the weight of the n th quantum rotation is effectively $2n$ (or $2n+1$) for large values of n . Weights such as n or $n+1$, which can only be maintained by very forced arguments, make (4.43) differ from Ehrenfest and Trkal by a factor 2, and are therefore almost certainly wrong.

The complete constant factor in these equations plays a part which is necessarily equivalent to the part played by the chemical constants of the various atoms and molecules. The chemical constants, therefore, must essentially depend on the weights of the lowest possible quantum states ((4.41) and (4.42)). The importance of the weights in this connexion appears to be inadequately appreciated, for the precise assumptions underlying the usual treatment are somewhat difficult to trace. It is better to postpone discussion of this point to § 11 after the equation of vapour-pressure has been considered at the close of this paper.

We have here displayed the various obvious approximate forms which we may expect the reaction-isobar to assume. Equation (4.12) is presumably, however, quite general, and the factor $B(T)$ should be very largely determinable from a study of the band spectrum—in particular, the band absorption spectrum. If this could be completely analysed at any one temperature, all the possible rotational and vibrational states of the molecule would be determined. It would then only remain to attach precise values to the weights to complete the specification of $B(T)$. It is just possible that a combined study of the reaction-isobar and the band spectrum might prove of considerable interest.

In conclusion, a possible objection may be raised to all the reasoning on which these results are based—namely, that it ignores radiation, whereas in fact a change of quantum state in the molecule probably seldom or never occurs without the emission or absorption of the appropriate radiation. It is, however, perfectly possible to include the temperature radiation in the statistical discussion, as has been shown elsewhere*. The results as functions of the temperature are unaffected, and the omission of an explicit account of the radiation in equilibrium with the dissociating gas is thus justified. The equilibrium is the same (as it must be) whether exchanges of energy take place by radiation or by collisions alone; but of course this does not imply that the equilibrium remains unaltered when the assembly is subjected to radiation of a different temperature from outside.

§ 5. *Mathematical discussion of the Dissociation Formulae.*—The evaluation of the integrals of § 3 proceeds just as in the simple cases of our first paper, with the addition that the asymptotic form of the series under the integral sign must be determined. If we write the integrand in the integral (3.5) for C in the form

$$\Sigma_N \frac{X!}{N! M! \sigma^N} [h_2(z)b(z)]^N [h_1(z)]^M z^{-N_X-E},$$

we see at once that every separate term is a product of power series† which obey all the conditions laid down in § 6 of our first paper. All that is there asserted of such power series can therefore equally be asserted of the sum Σ . Therefore the integrand on any circle γ has its maximum

* Darwin & Fowler, Proc. Camb. Phil. Soc. (1922).

† We ignore throughout the fact that $h_1(z)$, $h_2(z)$ are finally to be the limits of such series. The necessary refinements are easily made.

modulus on the real axis, and on the real axis has a unique minimum between 0 and 1 which is the sole such root of the equation

$$E = X\mathfrak{s} \frac{d}{d\mathfrak{s}} \log h_1(\mathfrak{s}) + \mathfrak{s} \frac{d}{d\mathfrak{s}} \log \sum_N \frac{X! \beta^N}{N! (X-2N)!} \quad (5.1)$$

We can then evaluate C to the approximation required when E and X are large by making the circle γ pass through $z=\mathfrak{s}$, and integrating over a small part of the circle in this neighbourhood. Further progress, however, obviously depends on a knowledge of the asymptotic form of $\log \sum_N$.

This series and all similar series that occur in such problems can be evaluated for real β by a study of the series in the neighbourhood of its maximum term. Moreover, only real values of β need be so studied; for the function represented by the series is an analytic function of the complex variables β or z near the positive real axis. To evaluate the integrals for C etc., we require the approximate values of this function on the circle γ near its intersection with the positive real axis. For this purpose it is sufficient to know the values of the first two (and sometimes more) differential coefficients of the function along γ at this point. These, however, are known when we know the corresponding differential coefficients along the real axis for real values of β or z .

For any real value of z there is a unique maximum among the terms of the series; for the ratio of consecutive terms of the series starts by being approximately βX^2 and steadily diminishes to β/X . If we refer to (4.1), we see that $\beta = f(z)/V$, where $f(z)$ is a function of z alone and independent of the number of systems in the assembly. Now we are considering the state of large assemblies, for which X is large. We have, therefore, to suppose that V is large, so that the ratio X/V is fixed. But in spite of this we can certainly arrange for X to be so large that $\beta X^2 > 1$ and $\beta/X < 1$ for any given value of z . Thus the terms start by increasing, and ultimately diminish without ever being able to increase again. There therefore exists a maximum which is unique.

The maximum occurs where two consecutive terms are as nearly equal as possible—that is, where

$$N = \beta(X-2N)(X-2N-1), \quad . \quad . \quad . \quad (5.11)$$

or with sufficient accuracy

$$N/M^2 = \beta(z). \quad . \quad . \quad . \quad . \quad (5.12)$$

In the further discussion the use of Stirling's formula appears to be for the first time unavoidable, but its use is easy to justify rigorously. We write

$$N = N_0 + \alpha, \quad M = M_0 - 2\alpha,$$

where α is an integer, and find that near the maximum term N_0 , M_0 , the terms of the series can be expressed in the form

$$\frac{1}{(2\pi)^{\frac{1}{2}}} \left(\frac{X}{M_0 N_0} \right)^{\frac{1}{2}} \exp \left\{ -\frac{1}{2} \alpha^2 \left(\frac{1}{N_0} + \frac{4}{M_0} \right) + N_0 \log \beta + X \log X - X \right. \\ \left. - N_0 \log N_0 + N_0 - M_0 \log M_0 + M_0 \right\}. \quad (5.2)$$

All other terms in (5.2) are of negligible order so long as α is confined to a certain stretch of values on either side of zero. This stretch can, however, be chosen so as to allow $\alpha \left(\frac{1}{N} + \frac{4}{M} \right)^{\frac{1}{2}}$ to range effectively from $-\infty$ to $+\infty$.

The terms in this strip provide the whole effective contribution to the series, and can be replaced by the integral of (5.2) with respect to α taken from $-\infty$ to $+\infty$. If we then write down $\log \Sigma_N$ and omit small terms, we obtain the asymptotic equality (X , V large)

$$\log \Sigma_N \frac{X! \beta^N}{N! (X-2N)!} = N_0 \log \beta + X \log X - X \\ - N_0 \log N_0 + N_0 - M_0 \log M_0 + M_0. \quad (5.3)$$

The integral (3.52) for $C\bar{N}$ can be treated in the same way. We find at once, to the same accuracy,

$$\Sigma_N \frac{NX! \beta^N}{N! (X-2N)!} = \beta \frac{d}{d\beta} \Sigma_N \frac{X! \beta^N}{N! (X-2N)!} \\ = N_0 \Sigma_N \frac{X! \beta^N}{N! (X-2N)!}. \quad (5.4)$$

If, now, we differentiate (5.3) with respect to β , we obtain

$$\beta \frac{d}{d\beta} \log \Sigma_N = N_0 + \beta \frac{\partial N_0}{\partial \beta} (\log \beta - \log N_0) - \beta \frac{\partial M_0}{\partial \beta} \log M_0 \\ = N_0, \quad \dots \dots \dots (5.41)$$

on using (5.12) and (3.21), which agrees with (5.4). This

proves that the asymptotic relation (5.3) can be differentiated with respect to β , and therefore also with respect to z .

Returning now to the integrals for C and $C\bar{N}$, it is easy to see how they are to be evaluated with the help of these asymptotic formulæ, and in particular that

$$\bar{N} = N_0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.5)$$

as determined by (5.12), provided that β is evaluated for the value of $\mathfrak{S}$ determined by (5.1). Thus the result $N/(\bar{M})^2 = \beta(\mathfrak{S})$ is obtained, which we have already discussed in § 4. We can now express (5.1) itself in more intelligible form, for it becomes, using (5.3) and (5.41),

$$E = X\mathfrak{S} \frac{d}{d\mathfrak{S}} \log h_1(\mathfrak{S}) + \bar{N}\mathfrak{S} \frac{d}{d\mathfrak{S}} \log \beta(\mathfrak{S}), \quad . \quad . \quad (5.6)$$

or

$$E = \bar{M}\mathfrak{S} \frac{d}{d\mathfrak{S}} \log h_1(\mathfrak{S}) + \bar{N}\mathfrak{S} \frac{d}{d\mathfrak{S}} \{ \log h_2(\mathfrak{S}) + \log b(\mathfrak{S}) \} - \bar{N}\chi. \quad . \quad . \quad (5.61)$$

This is precisely the form which the corresponding equation would take for an assembly in which N and M were *fixed* at their average values. We prove in the next section that the same is true of all details of the partition. The identification of $\mathfrak{S}$ with $e^{-1/\Lambda T}$ can be made by any of the methods of our former papers.

The changes in these results when the energy of radiation is accounted for may be mentioned here. It is found that the radiation has a partition function $R(z)$ which in the limit takes the form

$$R(z) = \exp \left\{ \frac{8\pi^3 V}{45c^3 h^3 (\log 1/z)^3} \right\}, \quad . \quad . \quad (5.7)$$

where c is the velocity of light. The only alteration in the formulæ is that the integrals for C etc. all contain a factor $R(z)$ in the integrand, and the equation (5.61) becomes

$$E = \bar{M}\mathfrak{S} \frac{d}{d\mathfrak{S}} \log h_1(\mathfrak{S}) + \bar{N}\mathfrak{S} \frac{d}{d\mathfrak{S}} \{ \log h_2(\mathfrak{S}) + \log b(\mathfrak{S}) \} + \mathfrak{S} \frac{d}{d\mathfrak{S}} \log R(\mathfrak{S}) - \bar{N}\chi. \quad . \quad (5.71)$$

As functions of $\mathfrak{S}$, the dissociation and the details of the energy partition are unaffected.

§ 6. *Further details of the partition.*—We have still to show that the possession of the values $\bar{N}$ and $\bar{M}$ is a “normal” property of the assembly; for this we should evaluate $\overline{(N-\bar{N})^2}$. We have at once

$$C\bar{N}^2 = \frac{1}{2\pi i} \int_{\gamma} \frac{dz}{z^{E+1}} [h_1(z)]^X \left(\beta \frac{d}{d\beta} \right)^2 \sum_N \frac{X! \beta^N}{N! (X-2N)!}, \quad (6.1)$$

and therefore, if we retain only terms of the highest order in X ,

$$\bar{N}^2 = (\bar{N})^2.$$

It follows at once that $\overline{(N-\bar{N})^2}$, which is equal to $\bar{N}^2 - (\bar{N})^2$, is of lower order than $(\bar{N})^2$, since the highest order terms cancel. This is sufficient by itself to prove that the possession of $\bar{N}$ is a normal property of the assembly. The actual evaluation of $\overline{(N-\bar{N})^2}$, though straightforward, is somewhat tedious, and we shall not attempt it here*.

We can discuss in the usual way the partition of energy. For example, consider the average amount of energy taken up by the internal motions and rotations of the molecules $[b(z)]$. In any particular example of the assembly with M atoms and N molecules the sum of all possible values of the energy on the $b(z)$ terms is

$$\frac{1}{2\pi i} \int_{\gamma} \frac{dz}{z^{E+1}} [h_1(z)]^M [h_2(z)]^N \left\{ z \frac{d}{dz} [b(z)]^N \right\} z^{-NX}.$$

This follows at once by comparison with our first paper; for the sum required is the same as $c\bar{e}_b$, say, where $\bar{e}_b$ is the mean value of E_b for this special example of the assembly. Summing for all examples of the assembly, we get

$$C\bar{E}_b = \frac{1}{2\pi i} \int_{\gamma} \frac{dz}{z^{E+1}} [h_1(z)]^X \left\{ z \frac{d}{dz} \log b(z) \right\} \sum_N \frac{NX! \beta^N}{N! (X-2N)!}, \quad (6.2)$$

and therefore

$$\bar{E}_b = \bar{N} \mathfrak{S} \frac{d}{d\mathfrak{S}} \log b(\mathfrak{S}), \quad (6.21)$$

where $\mathfrak{S}$ is given by (5.61). Similar results hold for the other energy terms. We thus find, as above, that the partition of energy is the same as if N and M were fixed at their average values.

* For all such questions see Darwin and Fowler, Proc. Camb. Phil. Soc. (Mich. 1922).

Consider further the distribution of molecules among the various states included in $b(z)$. Let p_r and ϵ_r be the weight and energy corresponding to the r th quantum state, and a_r the number of molecules in that state. In a particular example of the assembly the sum of all possible values of a_r is*

$$\frac{1}{2\pi i} \int_{\gamma} \frac{dz}{z^{E+1}} \{N p_r z^{\epsilon_r}\} [h_1(z)]^M [h_2(z)]^N [b(z)]^{N-1} z^{-N\chi}.$$

Summing for all examples of the assembly, we get

$$C a_r = \frac{1}{2\pi i} \int_{\gamma} \frac{dz}{z^{E+1}} [h_1(z)]^X \left\{ \frac{p_r z^{\epsilon_r}}{b(z)} \right\} \Sigma_N \frac{NX! \beta^N}{N! (X-2N)!} \quad (6.3)$$

Therefore

$$\bar{a}_r = \bar{N} p_r \mathfrak{S}^{\epsilon_r} / b(\mathfrak{S}), \quad . \quad . \quad . \quad (6.31)$$

with the usual value of $\mathfrak{S}$. Results similar in every way hold for the $h(z)$ factors †.

It is not necessary to suppose that the atoms and molecules of the X group are the only constituents of the assembly. We can suppose that any other systems in any quantity are also present, and, provided that no other reaction can occur, the extension of the whole of the preceding work is immediate. We can, for example, suppose that a constant volume perfect gas thermometer is also part of the assembly; if we do this we have at once one means of identifying $\mathfrak{S}$ with $e^{-1/kT}$.

It is interesting, in conclusion, to view the whole equilibrium condition from a somewhat different standpoint. For simplicity, we will think of the rotational and vibrational terms as separated, so that the rotational terms have their own separate partition function. Then, instead of thinking of the molecules as all of one kind with p different internal energies, we can regard them as p different types of molecule, between each two of which types there is a proper statistical equilibrium. This equilibrium by (6.31) takes the form

$$\bar{N}_1 / \bar{N}_2 = (p_1 / p_2) e^{-\chi_{12} kT}, \quad . \quad . \quad . \quad (6.4)$$

where χ_{12} is the excess of internal energy in the state 1 over that in state 2. This is here the reaction-isobar parallel to (4.1) for the case of dissociation. Moreover, it is easy to see that (6.4) is precisely what (4.1) must reduce to in a

* First paper, §§ 8, 9.

† Second paper, § 12.

reaction in which the total number of individuals does not change. The equilibrium conditions between the different types of molecules are exactly parallel to reaction-equilibria, and may be treated as such.

§ 7. *The temperature ionization of Hydrogen and similar problems.*—The degree of ionization in a gas of H-atoms* in statistical equilibrium is precisely analogous to the dissociation problem already treated†. It is convenient to discuss it here on account of its interest as the basis of Saha's work on stellar atmospheres; it raises also a practical difficulty of importance. It is convenient to consider the H-atom alone for the moment, since the structure and possible states of the H-atom may be regarded as completely known.

Consider an assembly of X H-nuclei and X electrons. These are now the elementary constituents, and the neutral H-atom is a complex—the molecule of our previous discussion—which can possess internal energy according to the orbit in which its electron is rotating. The masses of H and H^+ are the same, M , and the mass of the electron m . There are no relevant atomic rotations, and the symmetry numbers are all 1. If $b(z)$ is the partition function for the internal energy, we find, just as before, that the equilibrium state is

$$\bar{N}/(\bar{M})^2 = \beta(\mathfrak{S}), \quad \beta(\mathfrak{S}) = \frac{b(\mathfrak{S})}{\mathfrak{S}^2 \chi_h(\mathfrak{S})}, \quad \mathfrak{S} = e^{-1/kT}, \quad (7.1)$$

where N is the number of neutral atoms, M the number of free electrons or H-nuclei, χ the ionization potential in ergs, and $h(\mathfrak{S})$ the partition function for the motion of an electron.

When we come to specify $b(\mathfrak{S})$ we meet at once a fundamental difficulty. With the conventions of § 3 for zero energy, the atom possesses an apparently infinite series of possible states of energies $\epsilon_1, \epsilon_2, \dots, \epsilon_n, \dots$, where

$$\epsilon_n = \frac{2\pi^2 e^4 m}{h^2} \left(1 - \frac{1}{n^2}\right) = \chi \left(1 - \frac{1}{n^2}\right), \quad (7.2)$$

and e is the electronic charge. The weights of these possible

* The assembly must contain molecules H_2 in various states as well as atoms, but they will be negligible in number at the temperatures which are of interest in applications, and we may confine ourselves to the simpler problem here.

† On the assumption that free ions or electrons behave as a perfect gas. This assumption is open to attack, but is presumably correct at sufficiently low pressures.

states must be determined on the principles laid down by Bohr; they are * given by the formula

$$p_n = n(n+1). \quad . \quad . \quad . \quad . \quad (7.21)$$

Thus

$$b(\mathfrak{S}) = 2 + 6\mathfrak{S}^{X(1-2^{-2})} + 12\mathfrak{S}^{X(1-3^{-2})} + \dots \quad (7.22)$$

This series, however, can never converge † for any value of $\mathfrak{S}$, for $\epsilon_n \rightarrow \chi$ so that $\mathfrak{S}^{\epsilon_n} \rightarrow \mathfrak{S}^X$. The same difficulty would occur in discussing the reaction $X_2 \rightleftharpoons 2X$ if we supposed that there might be an infinity of possible quantized states of axial vibration with energies less than χ .

This difficulty is not merely analytical but real and physical; for this whole statistical calculation (and all others ever made) are based on the hypothesis that the systems of the assembly, though they occasionally interact so that exchanges of energy are possible, yet for the greater part of time are pursuing their own undisturbed motions with a definite energy of their own. It is only so that there can be a definite energy distribution to study statistically. But the radius (mean distance) of the n th orbit is given by the formula

$$a_n = \frac{n^2 h^2}{4\pi^2 m e^2} \quad . \quad . \quad . \quad . \quad . \quad (7.3)$$

and tends to infinity with n . The full development, therefore, of a single H-atom may require all space; and it is not possible that for a given concentration the fundamental hypothesis can be obeyed in the case of these outer orbits. If owing to the physical conditions of the assembly these outer orbits cannot exist for any appreciable time or perhaps cannot exist at all, they may be ignored altogether in the discussion of the energy distribution.

Pure statistical theory knows no half-way house between an impossible state which can be ignored and a state which is to receive its full share of energy—calculated of course on quantum or classical principles as the case may be. It is unlikely that this represents physical facts. The distributions given by statistical theory can only be limiting cases, and it is to be presumed that in reality there can often be a continuous transition between them. This can be represented by “faking” the weights, but we are

* Bohr, ‘The Quantum Theory of Line Spectra,’ p. 76, footnote.

† Herzfeld (*loc. cit.*) has previously pointed out this difficulty. His discussion, however, hardly overlaps that of this section.

then introducing arguments foreign to the pure theory which we have tried to develop here. The difficulty is discussed more fully in the next section. It is sufficient to say here that some modification of $b(z)$ must be made, which on physical grounds must be equivalent to cutting off the series more or less sharply after a certain number of terms. Exactly where it should be cut off is difficult to decide.

If we insert known values in (7.1) we obtain, in terms of the absolute temperature T , the total pressure P , and the fraction of atoms ionized x ,

$$\log \frac{x^2 P}{1-x^2} = -\frac{\chi}{kT} + 2.5 \log T + \log \left\{ \frac{(2\pi m)^{3/2} k^{5/2}}{h^3} \right\} - \log B(T), \quad \dots \quad (7.4)$$

which differs from Saha's formula in the term $B(T)$ alone.

Saha's formula, which is obtained thermodynamically, may be regarded as derived on the assumption that the H-atom is either ionized or in its lowest quantum state. On his premises, therefore, our $B(T)$ reduces to its first term p_1 . If p_1 could be equal to 1, then (7.4) would be in agreement with Saha's formula, and the latter would be valid so long as the neglect of the other states of the H-atom is justifiable, which may sometimes or indeed generally be the case. But it does not appear possible on Bohr's principles to accept the value 1 for p_1 . The true value is 2. The thermodynamic argument naturally, though of course not necessarily, forces in the value 1, as the idea of weight is somewhat foreign to it. We have here another example of the errors possible in a too uncritical use of the chemical constants.

In addition to a correction to Saha's formula for the error in p_1 , the occurrence of the rest of $B(T)$ (if any) must also be taken account of in applications of (7.4). The omission of this term by the thermodynamic argument is only apparent. It may be regarded thermodynamically as included in the specific heat term. But perhaps the present method has the advantage of putting it more clearly in evidence in proper relation to its origin; in the thermodynamic argument it is natural to think of all the gases concerned as perfect, and therefore to assume $C_p = \frac{5}{2}R$, forgetting that the equation does not follow if the atoms can take up internal energy. The degree of ionization at given temperature and pressure may possibly be modified by the presence of $B(T)$, which can be large at high temperatures if a large number of states are possible to

the H-atom. At the same time a large degree of ionization can already occur while the term χ/kT is still fairly large; in such a case a large number of states must be admissible if this correction is to be a serious one. Further re-discussion of the ionization formula cannot be undertaken in detail here.

§ 8. *The temperature equilibrium of a gas of H-atoms.*—To reduce the difficulty due to the possible infinity of states of the H-atom to its simplest form, consider the temperature equilibrium of a gas of neutral H-atoms in which no ionization is supposed to occur. Let $h(z)$ and $b(z)$ be the partition functions for the translatory and internal energies. The state of zero energy may be taken to be that in which the atoms are all at rest, with their electrons in their lowest quantum orbits. If we suppose that the allowable states of the atom are cut off after N terms, all the ordinary arguments apply for any value of N to such an assembly. Then the total number of weighted complexions representing the assembly is

$$C = \frac{1}{2\pi i} \int_{\gamma} \frac{dz}{z^{E+1}} [h(z)b(z)]^X. \quad (8.1)$$

If E_h and E_b are the mean values of the energy of translation and internal energy, then

$$\bar{E}_h = X \mathfrak{S} \frac{d}{d\mathfrak{S}} \log h(\mathfrak{S}) = \frac{3}{2} X kT, \quad (8.2)$$

$$\bar{E}_b = X \mathfrak{S} \frac{d}{d\mathfrak{S}} \log b(\mathfrak{S}), \quad (8.21)$$

$$\text{and } E = \bar{E}_h + \bar{E}_b.$$

Moreover,

$$b(\mathfrak{S}) = 2 + 6\mathfrak{S}^{X(1-2^{-2})} + \dots + N(N+1)\mathfrak{S}^{X(1-N^{-2})}, \quad (8.3)$$

$$\mathfrak{S}b'(\mathfrak{S}) = \chi \{ 6(1-2^{-2})\mathfrak{S}^{X(1-2^{-2})} + \dots + N(N+1)(1-N^{-2})\mathfrak{S}^{X(1-N^{-2})} \}. \quad (8.31)$$

Now if $\mathfrak{S}$ has any fixed value whatever, and we let $N \rightarrow \infty$, it is easy to see that

$$\frac{\mathfrak{S}b'(\mathfrak{S})}{b(\mathfrak{S})} \rightarrow \chi. \quad (8.4)$$

In spite, therefore, of the non-convergence of $b(\mathfrak{S})$, we can

arrive at a definite value for $\overline{E}_b$ without restriction to the number of terms; we have, in fact,

$$\overline{E}_b = X\chi. \quad (8.41)$$

This equality must hold in the limit for all values of $\mathfrak{S}$ (or T) except $\mathfrak{S}=0$, when we have obviously $\overline{E}_b=0$.

Consider more closely the implications of such a result. Given E , the temperature is to be determined by the equation

$$E = X\chi + \frac{3}{2}XkT.$$

This equation is impossible of fulfilment unless $E > X\chi$. The impossibility has of course entered in the limiting process $N \rightarrow \infty$. The equation must really mean that all the energy goes into lifting the electrons into orbits of high quantum numbers, the temperature remaining practically zero until enough energy ($X\chi$) has been supplied practically to ionize every atom. After that, on a further supply of energy, the usual kinetic energy of translation is built up with these already satiated atoms, no further internal energy being required. There does not seem to be any escape from these conclusions if the preceding analysis could really be pushed home without effective limitation on the possible states. In fact (granted the hypotheses) these conclusions seem to be in agreement with the dictates of common sense.

These conclusions of course cannot stand, and therefore restrictions on the possible states of the H-atoms are essential. We have already pointed out that the mean distance of the atoms provides such a limitation; for atoms of the size implied by the extended orbits must be able to exist sufficiently long for the equilibrium state to be set up. The tendency of the atom to radiate spontaneously, or under the stimulus of radiation, may also impose an additional control, which effectively cuts out high quantum number orbits from the statistical equilibrium.

§ 9. *General dissociation equilibria.*—We now return to the general dissociation problem, conforming as closely as possible to the treatment of Ehrenfest and Trkal. Consider an assembly of s different kinds of atoms, in number $X_1, \dots, X_s$, capable of forming j different kinds of molecules. In any example of the assembly let us suppose that there are $M_1, \dots, M_s$ free atoms of each sort and $N_1, \dots, N_j$ of each of the different molecules. Suppose in addition that the r th type of molecule, for example,

is composed of $q_{1r}, q_{2r}, \dots, q_{sr}$ atoms of the various types $1, \dots, s$, the q 's being all positive integers. Then

$$M_t + \sum_r q_{tr} N_r = X_t, \quad (t = 1, \dots, s). \quad (9.1)$$

Let the state of zero energy of the assembly be defined as that state in which all the molecules are dissociated and all the resulting atoms at rest. For a single molecule the state of zero energy is taken to be that of no motion of translation, no rotation, or the rotational quantum numbers zero, and no internal vibrations of any type, or all the vibrational quantum numbers zero*. Let χ_r be the heat of dissociation for the molecule of type r —that is, the constant work required to dissolve such a molecule at rest in its lowest quantum state into its separate component atoms also at rest. Let the partition functions be $g_1(z), \dots, g_s(z)$, $h_1(z), \dots, h_j(z)$ for the translational motion of the atoms and molecules, and $b_1(z), \dots, b_j(z)$ for the rotations and internal vibrations of the molecules: it is assumed that the series for the latter either converge or terminate. The symmetry numbers of the molecules are $\sigma_1, \dots, \sigma_s$. If the total energy of the assembly is E , and F is the energy for distribution by the partition functions when there exist $N_1, \dots, N_j$ molecules of the various types, then

$$F = E + \sum_r N_r \chi_r. \quad (9.2)$$

For any example of the assembly with $M_1, \dots, M_s$ atoms and $N_1, \dots, N_j$ molecules the number of weighted complexions c is given by

$$c = \frac{1}{2\pi i} \int_{\gamma} \frac{dz}{z^{E+1}} [g_1(z)]^{M_1} \dots [g_s(z)]^{M_s} [h_1(z) b_1(z)]^{N_1} \dots \times [h_j(z) b_j(z)]^{N_j}. \quad (9.3)$$

The number of different examples of such an assembly is †

$$\frac{X_1! \dots X_s!}{M_1! \dots M_s! N_1! \dots N_j! \sigma_1^{N_1} \dots \sigma_j^{N_j}}, \quad (9.31)$$

and therefore the total number of weighted complexions representing the assembly is

$$C = \frac{1}{2\pi i} \int_{\gamma} \frac{dz}{z^{E+1}} \sum_{(N)} \frac{X_1! \dots X_s! [g_1(z)]^{M_1} \dots [g_s(z)]^{M_s}}{M_1! \dots M_s! N_1! \dots N_j!} \times \left[\frac{h_1(z) b_1(z)}{\sigma_1 z^{X_1}} \right]^{N_1} \dots \left[\frac{h_j(z) b_j(z)}{\sigma_j z^{X_j}} \right]^{N_j}. \quad (9.32)$$

* As in § 4, it is easy to make the necessary modifications for the case in which zero values for any or all of these quantum numbers are to be excluded.

† Ehrenfest and Trkal, *loc. cit.* p. 169.

Using the equations (9.1), we can reduce this to the form

$$C = \frac{1}{2\pi i} \int_{\gamma} \frac{dz}{z^{E+1}} [g_1(z)]^{X_1} \dots [g_s(z)]^{X_s} \\ \times \Sigma_{(N)} \frac{X_1! \dots X_s! \beta_1^{N_1} \dots \beta_j^{N_j}}{M_1! \dots M_s! N_1! \dots N_j!}, \quad (9.33)$$

where

$$\beta_r = \frac{h_r(z) b_r(z)}{\sigma_r z^{X_r} \{g_1(z)\}^{q_{1r}} \dots \{g_s(z)\}^{q_{sr}}}, \quad (r=1, \dots, j). \quad (9.34)$$

The summation $\Sigma_{(N)}$ is to be taken over all possible values of $N_1, \dots, N_j$ —that is, over all zero and positive integral values which are small enough to leave the M 's positive or zero. In the same way,

$$C\overline{N}_r = \frac{1}{2\pi i} \int_{\gamma} \frac{dz}{z^{E+1}} [g_1(z)]^{X_1} \dots [g_s(z)]^{X_s} \\ \times \Sigma_{(N)} \frac{N_r X_1! \dots X_s! \beta_1^{N_1} \dots \beta_j^{N_j}}{M_1! \dots M_s! N_1! \dots N_j!}, \quad (r=1, \dots, j). \quad (9.35)$$

The series in (9.35) is obviously equal to

$$\beta_r \frac{\partial}{\partial \beta_r} \Sigma_{(N)},$$

where Σ_i is the series in (9.33), the equation for C .

To evaluate the integrals for C and $C\overline{N}_r$ we proceed as in § 5. By the arguments there used it follows from (9.32) that the integrand on any circle γ has its maximum on the real axis, and on the real axis has a unique minimum between 0 and 1 at $z=\mathfrak{S}$, where $\mathfrak{S}$ is the sole root of

$$E = \Sigma_i X_i \mathfrak{S} \frac{d}{d\mathfrak{S}} \log g_i(\mathfrak{S}) + \mathfrak{S} \Sigma_r \left\{ \frac{d\beta_r}{d\mathfrak{S}} \frac{\partial}{\partial \beta_r} \log \Sigma_{(N)} \right\}. \quad (9.4)$$

The discussion reduces as before to a study of the function $\log \Sigma_{(N)}$, which can be shown by an obvious extension of the former argument to possess a unique maximum term for values of the N 's determined by the equations

$$N_r / (M_1^{q_{1r}} M_2^{q_{2r}} \dots M_s^{q_{sr}}) = \beta_r, \quad (r=1, \dots, j). \quad (9.5)$$

These equations, j in number, with the s equations (9.1), are sufficient to determine the $(s+j)$ unknowns (M_i , N_r). In the neighbourhood of the maximum term (M_i^0 , N_r^0) the

terms of the series can be expressed to a sufficient approximation in the form

$$\frac{1}{(2\pi)^{1/2}} \left(\frac{X_1 \dots X_s}{M_1^0 \dots M_s^0 N_1^0 \dots N_j^0} \right)^{1/2} \exp \left\{ -\frac{1}{2} \sum_r \frac{\alpha_r^2}{N_r^0} \right. \\ \left. - \frac{1}{2} \sum_t \frac{(\sum_r q_{tr} \alpha_r)^2}{M_t^0} + \sum_r N_r^0 \log \beta_r + \sum_t (X_t \log X - X_t) \right. \\ \left. - \sum_r (N_r^0 \log N_r^0 - N_r^0) - \sum_t (M_t^0 \log M_t^0 - M_t^0) \right\}. \quad (9.51)$$

We can then, instead of summing the series, integrate (9.51) j times with respect to the α 's, and obtain with sufficient accuracy

$$\log \Sigma_{(N)} = \sum_r N_r^0 \log \beta_r - \sum_t (X_t \log X_t - X_t) \\ - \sum_r (N_r^0 \log N_r^0 - N_r^0) - \sum_t (M_t^0 \log M_t^0 - M_t^0). \quad (9.52)$$

For the series in $(\bar{N}_r)$ we obtain the same value as for $\Sigma_{(N)}$ multiplied by N_r^0 . If, further, we differentiate (9.52) partially with respect to β_1 say, we find

$$\beta_1 \frac{\partial}{\partial \beta_1} \log \Sigma_{(N)} = N_1^0 + \sum_r \beta_1 \frac{\partial N_r^0}{\partial \beta_1} (\log \beta_r - \log N_r^0) \\ + \sum_t \beta_1 \frac{\partial M_t^0}{\partial \beta_1} \log M_t^0.$$

If we express the $\partial M_t^0 / \partial \beta_1$ in terms of the $\partial N_r^0 / \partial \beta_1$ by using (9.1) we obtain coefficients of $\partial N_r^0 / \partial \beta_1$ which all vanish in virtue of (9.5). Thus

$$\beta_1 \frac{\partial}{\partial \beta_1} \Sigma_{(N)} = N_1^0 \Sigma_{(N)}, \quad (9.6)$$

and in general

$$\beta_r \frac{\partial}{\partial \beta_r} \Sigma_{(N)} = N_r^0 \Sigma_{(N)}, \quad (r=1, \dots, j). \quad (9.61)$$

This is in agreement with the result above, so that (9.52) can be differentiated with respect to any of the β 's and therefore with respect to z .

We have now all the necessary machinery to evaluate the partition, and find at once that $\bar{N}_r = N_r^0$, ($r=1, \dots, j$), provided that the β 's are evaluated for $z=9$. Thus the dissociation-equilibria must be determined by the j "laws

of mass-action" in the form

$$\overline{N}_r / \{ (\overline{M}_1)^{q_{1r}} \dots (\overline{M}_s)^{q_{sr}} \} = \frac{h_r(\mathfrak{S}) b_r(\mathfrak{S})}{\sigma_r \mathfrak{S}^{x_r} \{g_1(\mathfrak{S})\}^{q_{1r}} \dots \{g_s(\mathfrak{S})\}^{q_{sr}}},$$

$$(r=1, \dots, j). \quad (9.7)$$

Equation (9.4) relating the temperature and energy reduces to

$$E = \sum_t \overline{M}_t \mathfrak{S} \frac{d}{d\mathfrak{S}} \log g_t(\mathfrak{S}) + \sum_r \overline{N}_r \mathfrak{S} \frac{d}{d\mathfrak{S}} \{ \log h_r(\mathfrak{S}) + \log b_r(\mathfrak{S}) \} \\ - \sum_r \overline{N}_r \chi_r, \quad (9.71)$$

and the further details of the partition can be worked out exactly as in § 6. The result, that the details are the same as if the M 's and N 's were fixed at their equilibrium values, still holds.

It is convenient to express (9.7) in a form more in accord with the equivalent thermodynamical formulæ. We have for the whole assembly

$$PV = kT(\sum_t \overline{M}_t + \sum_r \overline{N}_r), \quad \dots \quad (9.8)$$

where P is the total pressure. If x_t , x_r^* are the "fractional concentrations"† of the various atoms and molecules respectively, then

$$x_t = \frac{\overline{M}_t}{\sum_t \overline{M}_t + \sum_r \overline{N}_r}, \quad x_r^* = \frac{\overline{N}_r}{\sum_t \overline{M}_t + \sum_r \overline{N}_r}. \quad (9.81)$$

We then express (9.7) in logarithmic form, eliminate $\overline{M}_t$, $\overline{N}_r$, and V by these expressions, and insert known values for $g_t(\mathfrak{S})$, $h_r(\mathfrak{S})$, and $\mathfrak{S}$. We obtain after reducing the equations

$$\sum_t q_{tr} \log x_t - \log x_r^* = (\sum_t q_{tr} - 1)(-\log P + \frac{5}{2} \log T) - \frac{\chi_r}{kT} \\ - \log B_r(T) + \sum_t q_{tr} \log \left\{ \frac{(2\pi m_t)^{3/2} k^{5/2}}{h^3} \right\} \\ - \log \left\{ \frac{(2\pi m_r^*)^{3/2} k^{5/2}}{\sigma_r h^3} \right\}, \quad (r=1, \dots, j). \\ \dots \quad (9.82)$$

In this equation $B_r(T)$ is the rotational and vibrational partition function expressed in terms of T , and m_t , m_r^* are the

† "Concentrations" is the term used by Ehrenfest and Trkal in this connexion. It is, however, not here used in its natural meaning of mass or number of molecules per c.c. Equation (9.82) is the reaction-isobar expressed effectively in terms of *partial pressures*.

masses of the atoms and molecules respectively. There may be, of course, a very large number of other mass-action equations among the constituents of the assembly, but they must all be expressible in terms of the j fundamental mass-action equations (9.7) or (9.82), in each of which only one complex constituent occurs. It is therefore unnecessary to consider such other equations in detail here.

In the cases considered by Ehrenfest and Trkal, $B_r(T)$ has its limiting form to which it approximates when the rotations are fully excited and the internal vibrations completely unexcited. In such cases (9.82) agrees with their results*.

Finally it is interesting to verify that the form of the reaction-isobar thus derived agrees with that derived by thermodynamic arguments from van't Hoff's equation,

$$\frac{d \log K}{dT} = -\frac{Q_p}{RT^2}, \quad \dots \quad (9.9)$$

where Q_p is the heat of reaction per gram-molecule at constant pressure and K the equilibrium constant; in particular, we shall see how the term $B(T)$ enters the reaction-isobar. By Kirchhoff's equation,

$$\frac{dQ_p}{dT} = -\sum q C_p, \quad \dots \quad (9.91)$$

where C_p is the specific heat at constant pressure, the summation is taken over all the reacting species, and q is the number of gram-molecules of each species with a negative sign for those that disappear. Therefore

$$\begin{aligned} Q_p &= Q_0 - \int_0^T \sum q C_p dT = Q_0 - \sum q RT - \int_0^T \sum q C_v dT, \\ &= Q_0 - \sum q RT - \sum q (U_v - (U_v)_0), \quad \dots \quad (9.92) \end{aligned}$$

where Q_0 is the limit of the heat of reaction as $T \rightarrow 0$ and U_v is the internal energy per gram-molecule at volume v . Therefore, on substituting in (9.9) and integrating, we have

$$\log K = \frac{Q_0}{RT} + \sum q \log T + \int_0^T \frac{dT}{RT^2} \sum q (U_v - (U_v)_0) + A, \quad (9.93)$$

where A is a constant. Equation (9.93) is the general thermodynamic formula. We can, however, translate it at once into our notation, and it then integrates in finite

* *Loc. cit.*, equation (41).

terms. For

$$Q_0/R = -\chi/k,$$

$$U_v - (U_v)_0 = N\mathfrak{S} \frac{d}{d\mathfrak{S}} \{ \log h(\mathfrak{S}) + \log b(\mathfrak{S}) \},$$

$$\frac{dT}{RT^2} = \frac{1}{N} \frac{d\mathfrak{S}}{\mathfrak{S}},$$

where N is Loschmidt's number. Thus

$$\log K = -\frac{\chi}{kT} + \Sigma q \log T + \Sigma q \{ \log h(\mathfrak{S}) + \log b(\mathfrak{S}) \} + A. \quad \dots (9.94)$$

Equations (9.94) and (9.82) are equivalent, except that in (9.82) the constant A is determined.

§ 10. *The vapour-pressure equation.*—We can derive in an exactly similar way the equation for the vapour-pressure of a solid—in particular, of a crystal. The contributions to the equation of the internal energy of the vapour molecule and the internal energy of the crystal can be formally included in the statistical discussion. It is not possible to include here a proper discussion of the partition function for a crystal without unduly lengthening this paper. This must be discussed elsewhere*. It is sufficient to point out that for a crystal of N molecules a partition function $[K(z)]^N$ can be constructed, based on Born and Karman's† results.

Following Ehrenfest and Trkal, we suppose that there are in the assembly N free molecules and a single crystal of M molecules. The molecules are composed out of s types of atom, $X_1, \dots, X_s$ in number, and there is a total of X molecules in all. The problem is actually one of dissociation-equilibrium in which there are only two kinds of molecule present—the actual free molecules N in number, and the whole crystal of which there is 1‡.

Let us suppose for definiteness that the assembly has zero energy when all the molecules are condensed on the crystal, and all the internal motions of the crystal vanish. We take our usual definition of zero energy for a free molecule, and suppose that χ is the work necessary to remove one molecule from the crystal when both crystal and molecule have (by convention) zero energy. It is easy to make the necessary modifications

* Darwin and Fowler, Proc. Camb. Phil. Soc. (1922).

† Born, *Der Dynamik der Krystallgitter*, p. 72.

‡ Or at least a number negligible compared with X .

if any of the corresponding quantum numbers cannot have the value zero. Then for any example of the assembly with N free molecules we have in the usual notation

$$F = E - N\chi, \quad \dots \dots \dots (10.1)$$

$$c = \frac{1}{2\pi i} \int_{\gamma} \frac{dz}{z^{E+1}} [K(z)]^M [b(z)h(z)]^N, \quad (10.11)$$

$$N + M = X.$$

The number of such examples of the assembly is

$$\frac{X_1! \dots X_s!}{N! \sigma^N 1! \sigma'}, \quad \dots \dots \dots (10.12)$$

where σ is the symmetry number of the free molecule and σ' the symmetry number of the crystal. Strictly speaking, there should also be included in (10.11) a partition function $H(z)$ for the mass motion of the whole crystal or crystals (Brownian movement), but this can obviously be ignored. The constant factor $(X_1! \dots X_s!)/\sigma'$ in (10.12) can also be dropped out. With these abbreviations, we have

$$c = \frac{1}{2\pi i} \int_{\gamma} \frac{dz}{z^{E+1}} [K(z)]^X \sum_N \frac{1}{N!} \left[\frac{b(z)h(z)z^X}{\sigma K(z)} \right]^N, \quad (10.2)$$

in which the summation goes from 0 to X . If X is taken sufficiently large, it is easy to show as usual that $\sum_N$ can be replaced for all purposes by its limit, which here has the simple form

$$\exp \left\{ \frac{b(z)h(z)z^X}{\sigma K(z)} \right\}. \quad \dots \dots \dots (10.21)$$

In the same way

$$cN = \frac{1}{2\pi i} \int_{\gamma} \frac{dz}{z^{E+1}} [K(z)]^X \left\{ \frac{b(z)h(z)z^X}{\sigma K(z)} \right\} \exp \left\{ \frac{b(z)h(z)z^X}{\sigma K(z)} \right\}, \quad \dots \dots (10.22)$$

and it follows at once that

$$\bar{N} = \frac{b(\mathfrak{z})h(\mathfrak{z})\mathfrak{z}^X}{\sigma K(\mathfrak{z})}, \quad \dots \dots \dots (10.3)$$

which is the vapour-pressure equation. In its more usual form it reads

$$\log p = -\frac{\chi}{kT} + \frac{5}{2} \log T + \log \left\{ \frac{(2\pi m)^{3/2} k^{5/2}}{\sigma h^3} \right\} + \log B(T) - \log K(T). \quad (10.31)$$

Ehrenfest and Trkal* give (10·31) in the form to which it reduces when $K(T)=1$, so that the energy of the crystal is ignored and $B(T)$ is replaced by its limit when all three rotations are excited, while all the internal vibrations are at rest.

§ 11. *The chemical constant.*—Equation (10·31) is the most satisfactory starting-point for a discussion of the chemical constant. The chemical constant may be defined † as the constant i of the vapour-pressure equation in the form

$$\log p = -\frac{\chi}{kT} + \frac{5}{2} \log T + i, \quad . \quad . \quad (11\cdot11)$$

for a monatomic gas or one which so behaves at the temperatures considered (H_2 at very low temperatures). For a diatomic gas with rotations fully excited, the equation becomes

$$\log p = -\frac{\chi}{kT} + \frac{7}{2} \log T + i', \quad . \quad . \quad (11\cdot12)$$

and for a triatomic gas with all three rotations excited

$$\log p = -\frac{\chi}{kT} + 4 \log T + i''. \quad . \quad . \quad (11\cdot13)$$

The heat content of the solid is neglected throughout for simplicity of statement; it can be included if desired.

If we apply the exact equation (10·31), putting $K(T)=1$, we can at once assign the theoretical value of i . The interesting case is (11·11). If the gas is genuinely monatomic, then $B(T)=1$, $\sigma=1$, and

$$i = \log \frac{(2\pi m)^{3/2} k^{5/2}}{h^3}, \quad . \quad . \quad . \quad (11\cdot2)$$

which is the usual well-known formula ‡. Suppose next that the gas is diatomic, and in the region in which the rotations are practically unexcited. Then for such a gas as H_2 , $\sigma=2$. If the state of no rotation is possible, then $B(T) \rightarrow 1$ and

$$i = \log \frac{(2\pi m)^{3/2} k^{5/2}}{2h^3}; \quad . \quad . \quad . \quad (11\cdot21)$$

* *Loc. cit.*, equations (85) and (46).

† Nernst, *Die theoretischen und experimentellen Grundlagen des neuen Wärmesatzes*, p. 136 (1918). Allowances, of course, can and should be made for the other terms varying with T which tend to zero as $T \rightarrow 0$.

‡ Nernst, *loc. cit.* p. 136.

if the state of no rotation is impossible, then

$$B(T) \sim p_1 e^{-\epsilon/kT}.$$

The term ϵ/kT must, as we saw in § 4, be absorbed in χ , and we are left with

$$i = \log \frac{p_1 (2\pi m)^{3/2} k^{5/2}}{2h^3}. \quad (11.22)$$

In such a case, therefore, the chemical constant may depend not only on the mass but also on the symmetry number and the weight of the lowest quantum state of the molecule.*

But we can draw certain interesting conclusions from the experimental data for H_2 in comparison with genuinely monatomic vapours. It is found† that the chemical constants for mercury, argon, zinc, cadmium, and hydrogen all agree within experimental error with the theoretical value calculated by formula (11.2). The fact that this formula holds for H_2 can only mean that formula (11.22) must be used with $p_1=2$. The inclusion of a factor $\frac{1}{2}$ or $\frac{3}{2}$ in the logarithm brings the value of i well outside the permissible range of error. We have, therefore, strong additional evidence (1) that the state of no rotation is impossible, and (2) that the weight of the one-quantum state of rotation is 2 and not 1 or 3. It is interesting to remark that it is only by a fortuitous cancelling of two errors that the formula for a monatomic gas is applicable to H_2 at all. It would be exceedingly interesting if the chemical constant of some non-symmetrical diatomic molecule could be determined in a region in which the rotations are practically unexcited. For such a molecule $\sigma=1$, and the chemical constant should be greater by $\log 2$ than the value derived from (11.2).

The theoretical values of i' and i'' are also given by Ehrenfest and Trkal. The value of i' can be obtained from the limiting form of $B(T)$ when the rotations are fully excited and the axial vibrations unexcited (see § 4). Thus

$$B(T) \sim \frac{8\pi^2 J k T}{h^2},$$

$$i' = \log \frac{4\pi (2\pi m)^{3/2} (2\pi J) k^{7/2}}{\sigma h^6}, \quad (11.3)$$

* The dependence on the symmetry number is pointed out by Ehrenfest and Trkal, *loc. cit.* p. 164.

† Nernst, *loc. cit.* p. 151; Egerton, *Phil. Mag.* vol. xxxix. p. 15 (1920).

which agrees with their value *. Agreement, however, is impossible if the weights n or $n+1$ are taken for the n th quantum state of the rotational motion. Such weights are therefore inadmissible, and there seems little doubt, in view of the additional evidence presented here, that $2n$ is the correct theoretical value of the weight of the n th quantum state for the rotations of a diatomic molecule. This molecule also, on the whole, fits best the demands of the curve of specific heats of H_2 †; but in this connexion one cannot discriminate between the weights $2n$ and n . The corresponding general value of i'' cannot at present be obtained from the limiting form of $B(T)$, for the quantized rotations of a rigid body with three unequal moments of inertia have not yet been completely worked out. It can, however, be obtained by treating the rotations throughout as obeying classical laws, as is done by Ehrenfest and Trkal. Its value is

$$i'' = \log \frac{8\pi^2(2\pi m)^{3/2}(8\pi^3 J_1 J_2 J_3)^{1/2} k^4}{\sigma h^6}, \quad \dots \quad (11.4)$$

where J_1, J_2, J_3 are the moments of inertia.

Returning to the dissociation equation (9.82), we see that the constant term in this equation is composed of the same chemical constants that occur in the vapour-pressure equations, and that no new constant enters. Equation (9.82) can be written, when the internal vibrations of the molecule are ignored and its rotations are either completely excited or unexcited,

$$\begin{aligned} \sum_t q_{tr} \log x_t - \log x_r^* = & -(\sum_t q_{tr} - 1) \log P + \alpha \log T \\ & + \sum_t q_{tr} i_t - i_r^*, \quad (r=1, \dots, j). \end{aligned} \quad (11.5)$$

In this equation α depends on how many rotations of the molecule are fully excited, and i_t, i_r^* are the chemical constants, according to the equations of this section, of the atoms and molecules respectively.

This brings to a conclusion the statistical theory of ordinary dissociation-equilibria. The theorems proved, which were summarized in § 1, have obviously a bearing on general thermodynamics, but this development cannot be undertaken here.

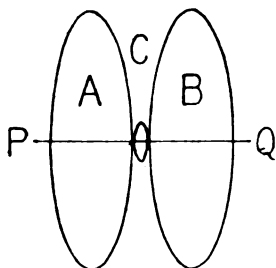
Cambridge, Aug. 1922.

* *Loc. cit.*, equation (46). † Reiche, *loc. cit.*

II. *The Process of Light Radiation from an Atom of a Gas leading to a Possible Interpretation of Planck's Quantum by means of Electrodynamics.* IV. By ALBERT C. CREHORE*.

SUPPOSE that the atom of fig. 1, which represents a section of a normal hydrogen atom as described in the first paper †, is one of the atoms in a mass of hydrogen gas in a vacuum tube in its steady state not emitting any characteristic light radiation, and that this gas is suddenly bombarded by a stream of negative electrons projected through it. Let us endeavour to trace the effect that one of these negative electrons passing near to a hydrogen atom of this kind, but not colliding with it, will have upon the atom merely because of the mutual dynamical action between the two bodies. The total effect may be studied by considering

Fig. 1.



Meridian section of the hydrogen atom described in the first paper.

independently the effects that the passing electron exerts upon the three individual charges making up the atom by means of the general expression for the ponderomotive force due to Saha that a second point charge in motion (the passing electron) exerts upon the first point charge (the separate individuals in the hydrogen atom). This force has been given in the first paper ‡ as

$$\mathbf{F} = \frac{E_1 E_2 (1 - \beta_2^2)}{k(RA_2)^3 (1 - \beta_1^2)^{\frac{1}{2}}} \left\{ \left(1 - \frac{1}{c^2} \mathbf{q}_1 \cdot \mathbf{q}_2 \right) \mathbf{R} - \frac{RA_1}{c} \mathbf{q}_2 \right\}, \quad (1)$$

* Communicated by the Author.

† Phil. Mag. Oct. 1921, p. 588.

‡ *Loc. cit.* Eq. (3), p. 570. This should read as in (1) above. An obvious misprint is the omission of the exponent 2 from the c in the term $\mathbf{q}_1 \cdot \mathbf{q}_2 / c^2$.

where the subscripts 1 and 2 refer to the first and second point charges respectively. The letters A_1 and A_2 are abbreviations for the expression $1 - \frac{q \cdot R}{cR}$ for the first and second points respectively.

For clearness of presentation let us at first neglect the fact that each individual body of charge is supposed to be a rotating body, and treat each simply as a static charge. Considering the positive charge of the atom ($+2e = E_1$) as a body at rest upon which we are to express the force due to the passing negative electron $-e$, we have

$$q_1=0, \beta_1=0, A_1=1, \text{ and } E_1 E_2 = -2e^2.$$

Hence (1) reduces to

$$F = -\frac{2e^2(1-\beta_2^2)}{k(RA_2)^3} \left\{ R - \frac{R}{c} q_2 \right\}, \quad \dots \quad (2)$$

An estimate of the probable value of the order of magnitude of q_2 , the velocity of the passing electron, may be obtained from the experimental observation that light radiation does not begin in hydrogen gas until the velocity of the passing electron corresponds to about 11 volts, that is to say a velocity of about 2×10^8 cm./sec., or $\beta_2 = \frac{2}{3} \times 10^{-2}$, less than the one hundredth part of the velocity of light. At this small velocity the part of the force expressed by the second term of (2) has less than one hundredth of the value of the part expressed by the first term, and may for a first approximation be neglected. If, therefore, we put also

$$q_2=0, \beta_2=0, \text{ and } A_2=1, \text{ (2) reduces to}$$

$$F = -\frac{2e^2}{kR^3} R, \quad \dots \quad (3)$$

which is merely the electrostatic force, this being an attraction, since by definition the vector R has its positive direction from the second to the first point charge.

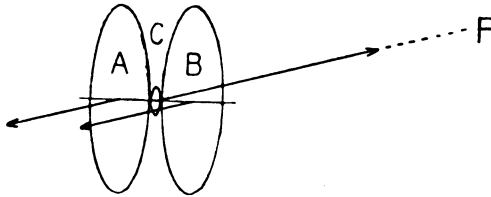
In a similar manner the force upon each individual negative electron of the atom becomes

$$F = \frac{e^2}{kR^3} R, \quad \dots \quad (4)$$

a repulsion of half the value of (3), being in the opposite

direction. These forces are represented in fig. 2 by vectors drawn from the centre of each charge of the atom parallel to **R**, that is to the line from the distant passing electron **P** to the atom. The sum of these forces is zero as far as any translational effect upon the atom as a whole is concerned, considering the three **R**'s to be approximately the same, but there is produced an internal effect within the atom itself. In general, unless **P** happens to be exactly in the equatorial plane of the atom, there is a component of each force which acts in the direction of its axis. The one pair of charges **B** and **C**, are held by this component more firmly together, while the other pair, **A** and **C**, are less firmly held and tend to separate. The chief effect of this component is, therefore, to increase the momentary pressure between **B** and **C**

Fig. 2.



Illustrating the forces upon the three parts of the atom due to the passing electron, **P**, electrostatic terms only.

and to decrease that between **A** and **C**, thus rendering **A** more readily detachable from the atom than **B** when other effects arise from any cause.

The other component of the forces resolved in the equatorial plane produces a couple tending to displace the two electrons **A** and **B** in the same direction off from the axis of **C**, but these electrostatic forces are not great enough to cause much displacement, and cannot be until the passing electron is near enough to be in contact with the atom. This near approach is not necessary to account for radiation from the atom, as will be shown.

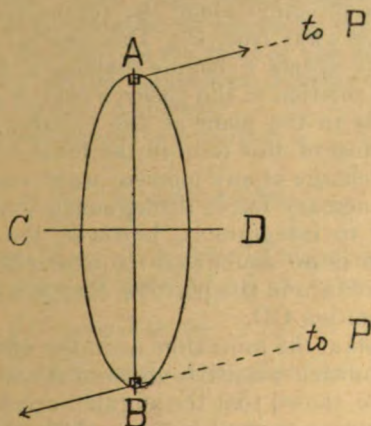
The rotation upon their axes of the charges **A**, **B**, and **C** having a non-spherical shape is the key to the behaviour of this atom. Let us next consider the effect that the passing electron **P** must have upon the positive charge **C** as a rotating charge. In fig. 3 the ellipse represents a meridian section of the positive charge, and **P** the distant passing

electron. Apply the formula (1) to find the force upon an element (dE_1) of the positive charge in its upper side at A due to the passing electron of charge $-e_2$ as point charges. For small velocities of P of the order of, say, the 1/100 the velocity of light, the quantities A_1 and A_2 in the general formula are approximately unity, and (1) becomes

$$\mathbf{F} = -\frac{e_2 dE_1}{kR^3} \left\{ \mathbf{R} - \frac{R}{c} \mathbf{q}_2 - \frac{\mathbf{q}_1 \cdot \mathbf{q}_2}{c^2} \mathbf{R} \right\} \quad \dots (5)$$

The first term within the brace, $\mathbf{R}$, is the electrostatic force discussed above acting along the line $\mathbf{R}$. The term $-\frac{R}{c} \mathbf{q}_2$ is

Fig. 3.



Illustrating the couple acting upon a pair of elements A and B of the positive charge due to the passing electron P originating in the term $(1/c^2) (\mathbf{q}_1 \cdot \mathbf{q}_2) \mathbf{R}$, which tends to rotate the axis CD.

small by comparison when β_2 is less than 1/100, and has a direction the same as $\mathbf{q}_2$, the velocity of P. Since the velocity, $\mathbf{q}_1$, of the first point A does not enter this expression, the force due to this term is substantially the same upon every element of the positive charge. This term, therefore, has the same kind of effect upon the positive charge as has the electrostatic force, only much smaller and in a different direction, so that the first two terms of (5) may be classed together and dismissed from further consideration, as merely producing a slight change in pressure between the electrons A and B upon C of the model (fig. 1).

The remaining term of (5) becomes the important one, and the effective force due to this term upon the element at A (fig. 3) due to P to produce a rotation of the axis CD, becomes

$$\mathbf{F} = -\frac{e_2 d E_1}{k R^3} \left\{ -\frac{\mathbf{q}_1 \cdot \mathbf{q}_2}{c^2} \mathbf{R} \right\}, \quad . \quad . \quad . \quad (6)$$

which is represented in the figure by the vector from A towards P, taking the direction of $-\mathbf{R}$. When the element A is moving either from or towards the observer perpendicular to the paper, then the motion of the element B diametrically opposite is in exactly the reverse direction. For this element the cosine of the angle between $\mathbf{q}_1$ and $\mathbf{q}_2$ has the opposite sign, and the force upon the element B has the opposite direction along $\mathbf{R}$, represented by the equal vector from B away from P. This pair of forces upon the two elements forms a couple having a tendency to turn the plane of rotation of the positive charge unless P happens to be exactly in the plane of the equator as a special case. The total effect of this term in the force equation (6) upon the positive charge at any moment is, of course, the integral of these elementary forces throughout its volume. Without undertaking to integrate it, however, the chief conclusion is that there is no doubt that the total effect of the motion of P is to produce in the positive charge a tendency to turn its axis of rotation CD.

There exists at the same time a similar effect of the passing electron upon each negative electron A and B in the atom; but it may be shown that the angular acceleration produced in these electrons is small in comparison with that produced in the positive charge, and therefore for the present purpose it is negligible.

To compare their orders of magnitude, consider a pair of elements of charge as before, and take the position of P on the axis so that the vector $\mathbf{R}$ is perpendicular to the plane of the orbit, and the effect is a maximum. The moment of the couple for two opposite elements, A and B of fig. 3, of the positive charge is then $2aF$, where a is the radius or distance from the element to the axis CD, and F the force upon it as expressed by (6). Setting this equal to the product of its moment of inertia I by the angular acceleration of the axis α , we find the angular acceleration in terms of the element of mass dm to be

$$\alpha = \frac{2aF}{I} = \frac{2F}{a dm} \quad . \quad . \quad . \quad (7)$$

Next suppose the negative electron to be divided up into the same number of elements as the positive charge, and select a pair of elements similarly situated in the oblate spheroid to those chosen in the positive charge. The elementary positive charge will then be twice as great as the elementary negative charge, because the whole positive charge is twice the negative electron. A similar expression may now be written for the angular acceleration of the negative elements, namely

$$\alpha' = \frac{2F'}{a'dm'} \quad \dots \dots \dots (8)$$

According to the mass-formula, the mass of a charge supposed spherical is inversely as its radius, the charge remaining the same. And, since each charge has been divided into the same number of elements, the masses of these elements are inversely as the radii of the said spheres, and again the radii of the spheres are directly as the radii of the two similarly placed elements.

Hence, for equal charges it is true that

$$\frac{a}{a'} = \frac{dm'}{dm}, \text{ or } a dm = a' dm' \quad \dots \dots \dots (9)$$

But for a positive charge of double the negative, since the radii vary as the squares of the charges, we have

$$a dm = 4a' dm' \quad \dots \dots \dots (10)$$

Hence the ratio of their angular accelerations by (7) and (8) is

$$\frac{\alpha}{\alpha'} = \frac{2F}{a dm} \times \frac{a' dm'}{2F'} = \frac{1}{4} \frac{F}{F'} \quad \dots \dots \dots (11)$$

But, by (6)

$$\frac{F}{F'} = \frac{dE_1}{dE_1'} \frac{q_1}{q_1'} = 2 \frac{q_1}{q_1'} = 2 \frac{\beta_1}{\beta_1'} \quad \dots \dots \dots (12)$$

Hence

$$\frac{\alpha}{\alpha'} = \frac{1}{2} \frac{\beta_1}{\beta_1'} \quad \dots \dots \dots (13)$$

But the gravitational equation, and the expression for the mass given in (68) of the first paper*, shows that the value of β for a ring equivalent to the positive charge of $2e$ is about 31.4 times the value of a corresponding ring equivalent to the negative electron. Hence the values of β for

* *Loc. cit.*

corresponding elements may be assumed to have this approximate ratio, and we have $\alpha = 15.7\alpha'$ showing that the angular acceleration produced by the passing electron in the two elements of the positive charge is about 16 times greater than that produced in the corresponding elements of the negative electron. The total integral effect for all elements in each of these two bodies may be assumed to have approximately this same ratio, and hence the effect upon the negative electrons as above stated may be neglected and attention centred upon the positive charge.

*The Effect of the Rotation of the Axis of the
Positive Charge.*

While it is true that this whole process cannot be worked out in exact detail because of the limitations of analysis, yet we are able to obtain a glimpse of what probably happens in a general way. If preferred, the processes now to be described may be regarded as assumptions, but with the understanding that they are clearly within the possibility of being substantiated by electrodynamics. Tracing the process as the passing electron has various velocities from zero up, it is clear that for a slow velocity the axis of C (fig. 1) may be turned slightly out of its normal position, the body of the positive charge rolling over smoothly on the surface of the electrons A and B without losing contact with them. Some energy must be taken from the passing electron if any alteration of this kind takes place in the atom. But whatever disturbance takes place upon the approach of the electron P, the normal condition is restored again as it departs, and all of the energy received is again returned to the electron, so that it passes the atom leaving with as much energy as it had upon approach.

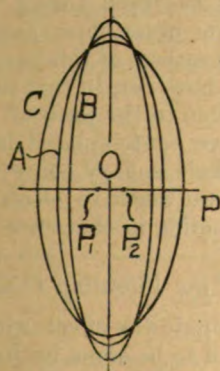
As the velocity of the passing electron becomes greater and greater the positive charge will be turned with more and more violence, and when the impulse is sufficient, it may turn with sufficient rapidity to leave contact with that electron, say A, whose pressure upon C is the least. This electron then returns and comes into actual collision with the positive charge, thereby setting up vibrations within its body that are characteristic of itself.

The case may be likened to rolling an elliptical wheel along a horizontal table. If the velocity of the wheel exceeds a definite critical value, the wheel will leave contact with the table, and upon its return bump against it, thus setting up sound waves. Some of the translational energy

of the wheel is then transformed into sound waves and is radiated out into space. So some of the translational energy of the passing electron is thus transformed in character into the high-frequency vibrations of the positive charge, and the energy thus transformed or received by the atom is not returnable to the passing electron because it has been thus transformed. This transformation and consequent reception of the energy by the atom is, therefore, only possible when the velocity of the passing electron exceeds a certain critical value, which prediction is in close accord with the known facts.

And further, just as is the case with the wheel set into vibration so as to emit waves of sound and thus radiate its energy into space to be reflected, refracted, and absorbed by all immediately surrounding objects, so the waves emitted by the vibrating positive charge are reflected from the objects surrounding it. The objects, however, immediately and practically completely surrounding it are the two negative electrons, A and B of fig. 1, and these effectively confine this received energy within the limits of the atom itself, none of it being radiated out into space because of these barriers.

Fig. 4.



Illustrating the change of shape when executing high-frequency vibrations natural to the positive charge. The effect of this vibration is taken as equivalent to two point charges, P_1 and P_2 , vibrating from and toward each other on the axis OP to a first approximation.

Whatever the details of this complicated process may be, at a certain critical velocity of the passing electron the positive charge may be set into vibration, say like that assumed in fig. 4. The normal figure of the rotating positive charge is tentatively represented in section by the

ellipse A, its axis of rotation being OP. The vibration may be supposed to change its shape between the extreme limits of the curves B and C. Since the volume is supposed to remain constant, the surface area changes, and there occurs an interchange of energy or oscillation between the potential energy and the rotational energy, the potential energy being associated with the surface pressure, or the surface tension if preferred. The whole energy content of the positive charge thus takes part in this vibration.

The actual vibration of the positive charge is probably far more complicated than that represented in fig. 4, and it is possible that the fundamental vibration there represented does not take place at all. It must be true, however, that the value of the natural free frequency of the positive ellipsoid regarded as a solid body far transcends any that has ever been measured, for it has the free period of the smallest known body. It is not material to the arguments that follow what the precise value of this frequency is, provided it is very great; that is to say, much greater than the highest frequencies observed anywhere, and probably having a wave-length comparable with the dimensions of the negative electrons themselves. When this is the case the energy of vibration may be prevented from escaping from the atom, for it has been shown* that bodies having dimensions close to the order of magnitude of the received waves become great absorbers of this radiation. The present case differs from this, however, in that the word "absorbed" implies a transformation in the form of the energy, whereas the phenomenon above contemplated is more analogous to total reflexion, the whole energy being confined within the region between the two negative electrons of the atom and without any transformation in character.

The Effect of the Vibrating Positive Charge.

Let us next investigate the effect which a single positive charge of $2e$, supposed to be alone by itself and in vibration as above described, would have upon a negative electron in its immediate neighbourhood. It may be stated here in advance of the demonstration that these high-frequency vibrations give rise to a new ponderomotive force, which may easily exceed in value the great electrostatic forces that heretofore have controlled the situation, and that these forces act in such a direction as to annul the electrostatic forces and overpower them to such an extent that a negative

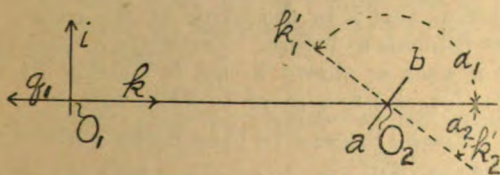
* L. Page, *Astrophys. J.* lii. p. 65, Sept. 1920.

electron may be driven away from its normal position in the atom.

To consider the positive charge as a vibrating oblate spheroid is beyond the power of analysis at the present time, but a first approximation may be made to the spheroid by substituting for it two vibrating points of charge of the same sign each equal to e . If the ellipsoid of fig. 4 is divided by the equatorial plane into two symmetrical halves and each half considered by itself, it is evident that the centre of volume of the charge of each half lies on the axis OP . These centres may be represented by the points P_1 and P_2 . As the charge changes its shape during the vibration, these centres will move from and toward each other along the axis OP . It is thought that to a first approximation the whole effect of the vibrating charge may be obtained by replacing the volume charge by two point charges, P_1 and P_2 , of the same sign and equal in value to half the positive charge.

This is not exactly the case of the electrical doublet upon which much work has been done because such doublets have been composed of charges of opposite sign, a positive and a negative charge. There has been no occasion heretofore, so far as is known, to treat of a doublet both parts of which have the same sign, and certainly such a case has never been treated by means of the Saha theory, which is used below. On this account it seems worth giving the demonstration quite fully.

Fig. 5.



Illustrating an electron at O_1 moving away from O_2 with velocity q_1 , and a positive point charge vibrating with harmonic motion along the line ab , and between these points as limiting distances from the origin, O_2 .

In fig. 5 let O_1 be the position of a negative electron, and let O_2 represent the centre of motion of a positive point charge, $+e$, moving with an harmonic motion along the line ab , and between these points as limiting distances from the origin, O_2 . It is required to find the average force upon the electron at O_1 , which may be supposed to be moving directly away from O_2 with velocity q_1 due to the force

originating in the harmonically vibrating positive charge at O_2 . Because of the small value of the rotation speed of the negative electron at O_1 , we shall regard it merely as a point charge in translational motion, and may select three rectangular axes i , j , and k , such that the k -axis takes the direction O_1O_2 , and the i -axis is in the plane determined by the line of vibration ab and the point O_1 , that is the plane of the paper.

In this situation the fundamental ponderomotive force equation (1) tells us that the total force upon the negative electron at O_1 must lie in the plane of the paper and have no component along the axis of j , since the force is the sum of two vectors in the direction of $\mathbf{R}$ and of $\mathbf{q}_2$, both of which always lie in the plane of the paper, the i - k -plane. Since the problem of finding the force of a complete continuous ring of charge upon another has been worked out, we shall follow the general plan there used and make reference to the equations in the first paper*.

In order to solve the case of the simple harmonic motion let us begin with a circular motion and suppose that the harmonic motion of the point along ab of fig. 5 is replaced by a uniform circular motion around a circle of diameter ab , the plane of which is perpendicular to the paper. This merely adds a second harmonic motion along the axis of j , so that the motion of the second point may be expressed as before (*loc. cit.* equation (5))

$$\mathbf{r}_2 = a_2(S_2 i' + C_2 j). \quad (14)$$

The k' -axis is then perpendicular to the plane of this circular motion, that is in the plane of the paper, and the j and j' axes coincide as before. The angle, α , is that between the k and k' axes as shown in fig. 5. Using the formulæ (8) and (9) (*loc. cit.*) $\mathbf{r}_2$ is given by (10), namely

$$\mathbf{r}_2 = a_2[S_2(\cos \alpha) i + C_2 j + S_2(\sin \alpha) k]. \quad (15)$$

And by differentiation $\mathbf{q}_2$ is as given by (16) of the first paper,

$$\mathbf{q}_2 = a_2 \omega_2 [C_2(\cos \alpha) i - S_2 j + C_2(\sin \alpha) k]. \quad (16)$$

The velocity of the first point, O_1 , is now, however, different, being motion along the k -axis, and may be represented by

$$\mathbf{q}_1 = -\beta_1 c k. \quad (17)$$

Hence

$$\frac{1}{c^2} \mathbf{q}_1 \cdot \mathbf{q}_2 = -\beta_1 \beta_2 C_2 \sin \alpha_1. \quad (18)$$

(in place of (17) *loc. cit.*)

* *Loc. cit.*

The vector $\mathbf{R}$ now becomes instead of (11) (*loc. cit.*)

$$\mathbf{R} = -\mathbf{r} - \mathbf{r}_2 \quad \dots \quad (19)$$

where

$$\mathbf{r} = z\mathbf{k} \text{ (instead of (6) } loc. cit.) \quad \dots \quad (20)$$

Hence by (15) and (20)

$$\begin{aligned} \mathbf{R} = & -a_2 S_2 (\cos \alpha) \mathbf{i} \\ & -a_2 C_2 \mathbf{j} \\ & + [-z - a_2 S_2 (\sin \alpha)] \mathbf{k}. \quad \dots \quad (21) \end{aligned}$$

Hence by (18) and (21)

$$\begin{aligned} \left(1 - \frac{1}{c^2} \mathbf{q}_1 \cdot \mathbf{q}_2\right) \mathbf{R} = & [-a_2 S_2 \cos \alpha - \beta_1 \beta_2 a_2 S_2 C_2 \sin \alpha \cos \alpha] \mathbf{i} \\ & + [-a_2 C_2 - \beta_1 \beta_2 a_2 C_2^2 \sin \alpha] \mathbf{j} \\ & + [-z - a_2 S_2 \sin \alpha - \beta_1 \beta_2 C_2 z \sin \alpha - \beta_1 \beta_2 a_2 S_2 C_2 \sin^2 \alpha] \mathbf{k}. \quad (22) \end{aligned}$$

By definition

$$A_1 = 1 - \frac{\mathbf{q}_1 \cdot \mathbf{R}}{cR}. \quad (\text{See (18) } loc. cit.)$$

Hence by (17) and (21)

$$\mathbf{q}_1 \cdot \mathbf{R} = \beta_1 cz + \beta_1 ca_2 S_2 \sin \alpha. \quad \dots \quad (23)$$

Whence

$$\frac{RA_1}{c} = \frac{R}{c} - \frac{\beta_1}{c} (z + a_2 S_2 \sin \alpha), \quad \dots \quad (24)$$

(instead of (19) *loc. cit.*)

The whole force upon the first point due to the second may now be found by substituting in (1) the expressions (22) and (24), giving

$$\begin{aligned} \mathbf{F} = & \frac{(-e_1)(+e_2)(1-\beta_2^2)}{k(RA_2)^3(1-\beta_1^2)^{\frac{1}{2}}} \{ [-a_2 S_2 \cos \alpha - R\beta_2 C_2 \cos \alpha \\ & + \beta_1 \beta_2 z C_2 \cos \alpha] \mathbf{i} \\ & + [-a_2 C_2 - \beta_1 \beta_2 a_2 \sin \alpha + R\beta_2 S_2 - \beta_2 \beta_2 z S_2] \mathbf{j} \\ & + [-z - a_2 S_2 \sin \alpha - R\beta_2 C_2 \sin \alpha] \mathbf{k} \} \quad \dots \quad (25) \end{aligned}$$

In this equation the distance a_2 is extremely small, being less than 10^{-10} cm., which is the order of magnitude of the positive charge, and we are only interested in the value of the force when R is large as compared with a_2 , in those terms which vary as the inverse square of the distance, which are large as compared with higher orders in R .

Except for the R which appears indirectly in (25) through the sines and cosines, S_2 and C_2 , it is correct to use the approximation that $R=s=r$. And, since O_2 is located on the k -axis in this particular case, $x=y=0$, and $r=z$. Therefore, omitting all terms not containing R or z in (25), as contributing nothing to the inverse square terms, and replacing x , y , and z by the direction-cosines X , Y , and Z , namely $X=Y=0$, and $Z=1$, (25) reduces to the following instead of (30) (*loc. cit.*):

$$\mathbf{F} = \frac{(-e_1)(+e_2)(1-\beta_2^2)r}{k(RA_2)^3(1-\beta_1^2)^{\frac{1}{2}}} \left\{ \begin{aligned} &[-\beta_2(1-\beta_1)C_2 \cos \alpha] i \\ &+ [\beta_2(1-\beta_1)S_2] j \\ &+ [-1-\beta_2C_2 \sin \alpha] k \end{aligned} \right\}, \quad (26)$$

where as in (31) (*loc. cit.*)

$$(RA_2)^{-2} = \left[1 + 3\beta_2 \left(\frac{v}{r}\right) + 6\beta_2^2 \left(\frac{v}{r}\right)^2 + 10\beta_2^3 \left(\frac{v}{r}\right)^3 + \dots \right] r^{-3}. \quad (27)$$

Corresponding to (21) and (22) (*loc. cit.*) the value of RA_2 becomes

$$\begin{aligned} RA_2 &= R - \frac{q_2 \cdot \mathbf{R}}{c} = R - \beta_2 [-zC_2 \sin \alpha] \\ &= R - \beta_2 v, \end{aligned} \quad (28)$$

where

$$v = -zC_2 \sin \alpha \quad (29)$$

and

$$\frac{v}{r} = -C_2 \sin \alpha, \text{ for use in (27).} \quad (30)$$

Equation (26) gives the whole force of the charge, $+e_2$, revolving in a circular orbit upon the negative electron, $-e_1$, moving along the axis of k . If the charge $+e_2$ is changed into an elementary charge dE_2 , the expression becomes the equivalent of (42) (*loc. cit.*)* and may be integrated around the closed ring so as to give the whole force of the ring upon the retreating electron in a manner similar to that employed in the first paper. Although the distance r is now a function of time, whereas it was independent of time in the former example, yet this integration is made for one instant of time, and time is not the variable. The result of

* The r which appears in the denominator of (42) (*loc. cit.*) is a misprint. It should have been in the numerator of the coefficient as in (26) above.

the integration around the circle gives the force upon the electron due to the ring as follows :

$$\mathbf{F} = \frac{(-e_1)(+e_2)(1-\beta_2^2)}{kr^2(1-\beta_1^2)^{\frac{1}{2}}} \left\{ [\beta_2^2(1-\beta_1) \sin \alpha \cos \alpha \right. \\ \left. + \frac{3}{2}\beta_2^4(1-\beta_1) \sin^3 \alpha \cos \alpha] i \right. \\ \left. + [-1 - \frac{1}{2}\beta_2^2 \sin^2 \alpha - \frac{3}{8}\beta_2^4 \sin^4 \alpha \dots] k \right\}. \quad (31)$$

This corresponds to the final expression (57) in the first paper, which is the force of one ring upon another. By making $X=Y=0$, $Z=1$, and $\xi=X \cos \alpha + Z \sin \alpha = \sin \alpha$ in that equation we obtain (31) exactly except for the factor $(1-\beta_1)$ in the i -component. The presence of this β_1 -term here is due to the new condition imposed, namely that the electron at O_1 in fig. 5 is in translational motion instead of being at rest relative to the centre O_2 .

The force upon the electron at O_1 contributed by each and every element of this ring when averaged for time over a complete revolution or many revolutions must be the same as that due to any other element, provided the distance r does not change during one revolution. Consequently (31) expresses the average force upon the electron equally well whether the second charge is a single point revolving in a circle or whether it is a charge of the same amount uniformly distributed around the circle, provided the speed $\beta_1 c$ is zero. Moreover, it is clear that, if the distance r changes but little during a complete revolution of the point at O_2 as compared with its total value, then (31) may represent the average force upon the electron at O_1 even though it be in motion and β_1 is not zero. It may now be recalled that the frequency of revolution of the charge at O_2 is supposed in our example to be very great so that the wave-length of the radiated waves is comparable with the dimensions of the negative electron itself. This means that O_1 would only advance a distance comparable with its own dimensions even though it has a velocity as great as that of light, and this would make very little change in the distance r during a complete period. For this reason (31) may be taken to represent the average force upon O_1 with great approximation, even though its velocity is not small. But our problem is to find the effect of a simple harmonic motion of the point at O_2 upon the electron at O_1 .

The circular motion of the charge at O_2 may be represented as the sum of two simple harmonic motions, the one

in the plane of the paper in fig. 5 and the other perpendicular to the paper. As above stated, the original equation (1) shows that the total force upon O_1 due to any kind of motion of O_2 confined to the plane of the paper, the i - k -plane, contributes no component of force upon O_1 in a direction perpendicular to this plane, the j -axis. Similarly it may be shown that any kind of motion of O_2 along the j -axis alone contributes a force upon O_1 along this same j -axis only due to such motion. The electrostatic part of the force is, of course, along the k -axis in every case. This may easily be shown because the term $\mathbf{q}_1 \cdot \mathbf{q}_2$ in (1) vanishes when the two velocities are perpendicular to each other as now supposed, and the whole force, therefore, takes the direction of $\mathbf{q}_2$ along the j -axis with the exception of the first or electrostatic term of (1).

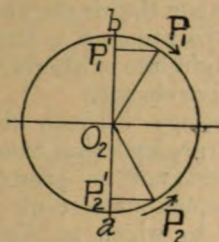
Now there is no j -component of the force in (31) above, which represents the result for circular motion, and since the component of this motion in the plane of the paper, fig. 5, can give no j -component, and the j -component is absent, it follows that the component harmonic motion along the j -axis contributes nothing at all to the total average force. The conclusion is that (31) represents equally well the average force upon the electron at O_1 whether the motion of the charge at O_2 is circular motion in a plane perpendicular to the paper in fig. 5 having a diameter ab , or is simple harmonic motion along the line ab . Hence (31) is the complete result for simple harmonic motion sought. The method employing the ring, which has been used above, seems to present less difficulty in effecting the integrations than would be the case were the time used as the independent variable, but the result must be the same.

The Effect of Two Vibrating Positive Charges.

In the problem just considered the vibrating charge at O_2 may be taken to represent, as above pointed out, one half only of the vibrating positive charge of the hydrogen atom. The other half vibrates in a similar manner with the same amplitude and frequency but in a different phase. The point P_1 in fig. 6 may represent the point above discussed revolving in the clockwise sense so that its projection P_1' describes the harmonic motion along ab . The other half of the positive charge may then be represented by a point, P_2 , making the same angle with the diameter ab at all times and revolving in the counterclockwise sense, its projection being at P_2' describing harmonic motion along

the same diameter ab . To thus reverse the direction of rotation in the circle is equivalent to changing the direction of the axis of rotation through 180° in fig. 5 from the direction k_1' to that of k_2' , thus changing the angle α_1 into α_2 , the latter being the supplement of the former. Hence $\sin \alpha_1 = \sin \alpha_2$ and $\cos \alpha_1 = -\cos \alpha_2$.

Fig. 6.



Illustrating the opposite phases of the two points P_1 and P_2 of fig. 4.

The average force of the second vibrating point at O_2 in fig. 5 is, therefore, given by the same equation (31) by reversing the sign of the cosine but not that of the sine. This reverses the sign of the i -component but does not affect that of the k -component. In taking the sum of the forces due to both halves of the positive charge in harmonic motion, therefore, the i -component cancels and the k -component is double that expressed in (31). The total average force of the positive vibrating charge is then

$$F = \frac{2e^2(1-\beta_2^2)}{kr^2(1-\beta_1^2)^{\frac{1}{2}}} (1 + \frac{1}{2}\beta_2^2 \sin^2 \alpha + \frac{3}{8}\beta_2^4 \sin^4 \alpha + \dots) k. \quad (32)$$

Since the series in the last parenthesis is the development of $(1-\beta_2^2 \sin^2 \alpha)^{-\frac{1}{2}}$, the complete force may also be written

$$F = \frac{e^2}{kr^2(1-\beta_1^2)^{\frac{1}{2}}} \left[\frac{2(1-\beta_2^2)}{(1-\beta_2^2 \sin^2 \alpha)^{\frac{1}{2}}} \right] k. \quad (33)$$

The Effect of the Hydrogen Ion upon an Electron.

The hydrogen ion is obtained by adding a negative electron to the positive charge above considered. By the fundamental equation (1) the force that this extra electron exerts upon the electron at O_1 , fig. 5, is

$$F = -\frac{e^2}{kr^2(1-\beta_1^2)^{\frac{1}{2}}} k. \quad (34)$$

in the plane of the paper in fig. 5 and the other perpendicular to the paper. As above stated, the original equation (1) shows that the total force upon O_1 due to any kind of motion of O_2 confined to the plane of the paper, the i - k -plane, contributes no component of force upon O_1 in a direction perpendicular to this plane, the j -axis. Similarly it may be shown that any kind of motion of O_2 along the j -axis alone contributes a force upon O_1 along this same j -axis only due to such motion. The electrostatic part of the force is, of course, along the k -axis in every case. This may easily be shown because the term $\mathbf{q}_1 \cdot \mathbf{q}_2$ in (1) vanishes when the two velocities are perpendicular to each other as now supposed, and the whole force, therefore, takes the direction of $\mathbf{q}_2$ along the j -axis with the exception of the first or electrostatic term of (1).

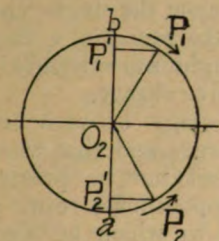
Now there is no j -component of the force in (31) above, which represents the result for circular motion, and since the component of this motion in the plane of the paper, fig. 5, can give no j -component, and the j -component is absent, it follows that the component harmonic motion along the j -axis contributes nothing at all to the total average force. The conclusion is that (31) represents equally well the average force upon the electron at O_1 whether the motion of the charge at O_2 is circular motion in a plane perpendicular to the paper in fig. 5 having a diameter ab , or is simple harmonic motion along the line ab . Hence (31) is the complete result for simple harmonic motion sought. The method employing the ring, which has been used above, seems to present less difficulty in effecting the integrations than would be the case were the time used as the independent variable, but the result must be the same.

The Effect of Two Vibrating Positive Charges.

In the problem just considered the vibrating charge at O_2 may be taken to represent, as above pointed out, one half only of the vibrating positive charge of the hydrogen atom. The other half vibrates in a similar manner with the same amplitude and frequency but in a different phase. The point P_1 in fig. 6 may represent the point above discussed revolving in the clockwise sense so that its projection P_1' describes the harmonic motion along ab . The other half of the positive charge may then be represented by a point, P_2 , making the same angle with the diameter ab at all times and revolving in the counterclockwise sense, its projection being at P_2' describing harmonic motion along

the same diameter ab . To thus reverse the direction of rotation in the circle is equivalent to changing the direction of the axis of rotation through 180° in fig. 5 from the direction k_1' to that of k_2' , thus changing the angle α_1 into α_2 , the latter being the supplement of the former. Hence $\sin \alpha_1 = \sin \alpha_2$ and $\cos \alpha_1 = -\cos \alpha_2$.

Fig. 6.



Illustrating the opposite phases of the two points P_1 and P_2 of fig. 4.

The average force of the second vibrating point at O_2 in fig. 5 is, therefore, given by the same equation (31) by reversing the sign of the cosine but not that of the sine. This reverses the sign of the i -component but does not affect that of the k -component. In taking the sum of the forces due to both halves of the positive charge in harmonic motion, therefore, the i -component cancels and the k -component is double that expressed in (31). The total average force of the positive vibrating charge is then

$$F = \frac{2e^2(1-\beta_2^2)}{kr^2(1-\beta_1^2)^{\frac{1}{2}}} \left(1 + \frac{1}{2}\beta_2^2 \sin^2 \alpha + \frac{3}{8}\beta_2^4 \sin^4 \alpha + \dots\right) k. \quad (32)$$

Since the series in the last parenthesis is the development of $(1-\beta_2^2 \sin^2 \alpha)^{-\frac{1}{2}}$, the complete force may also be written

$$F = \frac{e^2}{kr^2(1-\beta_1^2)^{\frac{1}{2}}} \left[\frac{2(1-\beta_2^2)}{(1-\beta_2^2 \sin^2 \alpha)^{\frac{1}{2}}} \right] k. \quad (33)$$

The Effect of the Hydrogen Ion upon an Electron.

The hydrogen ion is obtained by adding a negative electron to the positive charge above considered. By the fundamental equation (1) the force that this extra electron exerts upon the electron at O_1 , fig. 5, is

$$F = -\frac{e^2}{kr^2(1-\beta_1^2)^{\frac{1}{2}}} k. \quad (34)$$

If this is added to (33) the force upon the electron due to the ion is as follows :

$$F = \frac{e^2}{kr^2(1-\beta_1^2)^{\frac{1}{2}}} \left[-1 + \frac{2(1-\beta_2^2)}{(1-\beta_2^2 \sin^2 \alpha)^{\frac{1}{2}}} \right] k. \quad (35)$$

The combination of this ion with the negative electron at O_1 would make a neutral hydrogen atom, so that (35) represents the force upon the single electron which is being driven away from the atom in a straight line because of these new forces brought into existence by the high-frequency vibration of the positive charge.

Of course the analogy between this hypothetical case employing point charges and that where the electrons have finite dimensions must not be pressed too far, but it is believed that this approximate result will assist in understanding the process by which an electron may be driven out from its normal position in the atom to a maximum distance and back again in a straight line, thus radiating energy out into space and away from the atom. These equations seem worth examining in some detail on this account.

Let us first illustrate how the force depends upon the angle, α , shown in fig. 5, when other quantities are constant. When the forces in (33) for the positive charge and in (35) for the ion acting upon the negative electron at the distance, r , are plotted as polar curves with F and α as the only variables, a system of curves is obtained by giving to β_2 a succession of values, one curve for each value. It will be remembered that $\beta_2 c$ represents the maximum velocity of the harmonic motion of the vibrating points, P_1 and P_2 , which have been taken as equivalent to the positive charge, and there is reason to think that this velocity may be very great initially, even close to the velocity of light, but that it decreases with time as the amplitude decreases with loss of energy because of the translational motion of the electron, and passes continuously through all values from its maximum down to its final velocity.

A system of six curves representing the force upon the electron due to the positive charge alone is shown in fig. 7 for the numerical values of β_2 , 0, 0.5, $\sqrt{2}/2 = 0.707$, 0.8, $\sqrt{3}/2 = 0.866$ and 0.9 according to (33), which is the polar equation of an ellipse as regards the variables F and α . When $\beta_2 = 0$, the curve is a circle, since the force is merely the electrostatic force of attraction equal in all directions.

The radius of this circle is

$$2 \frac{e^2}{kr^2(1-\beta_1^2)^{\frac{1}{2}}} \quad \dots \quad (36)$$

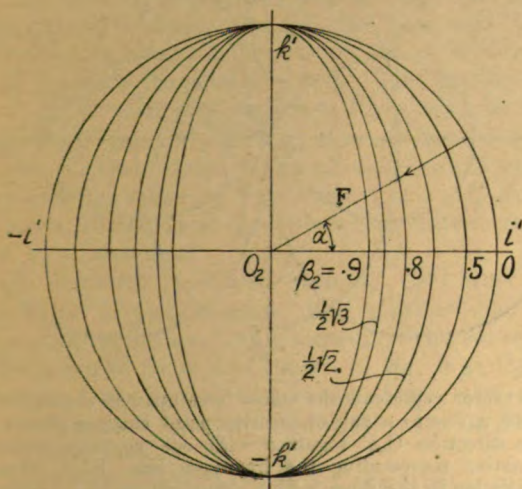
When $\beta_2=0.5$, the major axis of the ellipse is

$$\sqrt{3} \frac{e^2}{kr^2(1-\beta_1^2)^{\frac{1}{2}}}, \quad \dots \quad (37)$$

and the minor axis

$$\frac{3}{2} \frac{e^2}{kr^2(1-\beta_1^2)^{\frac{1}{2}}} \quad \dots \quad (38)$$

Fig. 7.

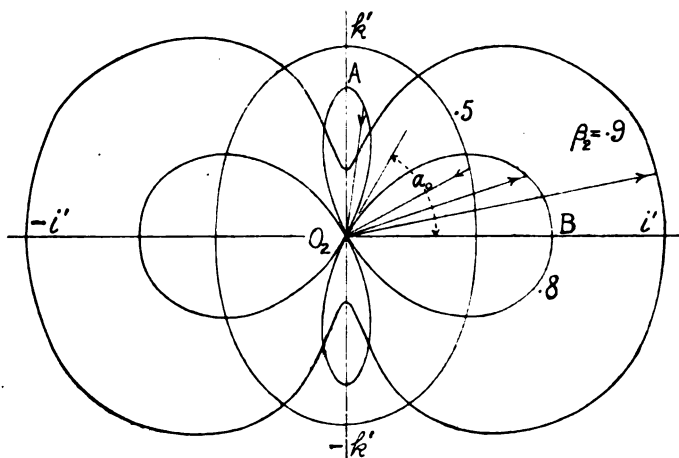


The radius vector from the curve to the origin O_2 represents the whole attractive force upon the electron at a fixed distance, r , due to a pair of positive point charges at O_2 vibrating in the direction O_2K' . Each ellipse shows the change in the force with the change in the angle α (see fig. 5), other quantities being constant. The six ellipses correspond to six different values of β_2 shown.

The major axes of all the ellipses are made equal to each other in the figure because the shape of the curve is the important feature rather than absolute values. The matter may be adjusted by supposing either that the scale of the drawing is changed in the above case in the ratio of $\sqrt{3}$ to 2, or that β_1 has different values in each of the curves. In the case when $\beta_2=0.5$, $1-\beta_1^2$ may be changed in the ratio 4 to 3 in order that the major axis may have the same value as the radius of the circle for $\beta_2=0$.

The force due to the ion (35) in distinction to the positive charge alone is also represented by a circle when $\beta_2=0$, since it becomes the electrostatic force of half the value of (36). Three curves are shown in fig. 8 representing the force due to the ion corresponding to $\beta_2=0.5$, 0.8 , and 0.9 plotted from (35). They may be constructed

Fig. 8.



The radius vector represents the whole force upon an electron at a fixed distance, r , due to a pair of positive point charges at O_2 vibrating in the direction O_2k' together with one negative electron, the combination representing the hydrogen ion. Each curve shows the variation in the force with a change in the angle α (see fig. 5), other quantities being constant. When $\beta_2=0.5$ the force is attractive at all angles. At $\beta_2=0.8$ the force is attractive in the loop A and repulsive in the loop B. When $\beta_2=0.9$ the force is repulsive at all angles.

graphically from the corresponding ellipses of fig. 7 by subtracting a constant value from the radius vector of the ellipse equal in amount to the first term of (35). When $\beta_2=0.5$, the force is still attractive at all angles α , but is greatest along the polar direction O_2k' and least along the equatorial direction O_2i' .

When $\beta_2=0.8$, the force is still an attraction along the polar direction following the loop curve O_2A , but is a repulsion in the equatorial area within the loop O_2B . In this case there exists a critical angle, α_0 , at which the whole force

vanishes. This angle is obtained by equating (35) to zero, giving

$$\frac{1-\beta_2^2}{(1-\beta_2^2 \sin^2 \alpha_0)^{\frac{1}{2}}} = \frac{1}{2}, \quad \dots \quad (39)$$

or

$$\sin^2 \alpha_0 = 8 - 4\beta_2^2 - \frac{3}{\beta_2^2}. \quad \dots \quad (40)$$

When $\beta_2 = 0.8$, $\sin^2 \alpha_0 = 0.7525$, $\sin \alpha_0 = 0.8675$ approx., and $\alpha_0 = 60^\circ 10'$.

It is evident from the general expression in (39) that the force-curve will have two branches or loops, the one representing attractive forces nearer the pole and the other repulsive forces nearer the equator for a certain limited range of β_2 , such that $\sin \alpha$ is real. The smallest possible value of β_2 to give any repulsive force may be found by making $\alpha = 0$ in (39), giving $\beta_2 = \sqrt{2}/2 = 0.707$ approx. The curve obtained from (35) with this critical value of β_2 is shown in fig. 9 having two loops, O_2k' , $-O_2k'$, showing a maximum attraction at the pole which falls to zero on the equator, a critical case.

As β_2 increases it is also seen by (39) that a second critical value is passed when $\beta_2 = \sqrt{3}/2 = 0.866$ approx., corresponding to $\sin \alpha = 1$ and $\alpha = \pi/2$. The curve obtained with this value of β_2 is also shown in fig. 9 at O_2i' , $-O_2i'$, representing two loops of repulsive force, the maximum being now on the equator, falling to zero at the pole, a second critical case.

As β_2 becomes larger than $\sqrt{3}/2$ the force is repulsive at all angles. At $\beta_2 = 0.9$ the curve marked 0.9 in fig. 8 is obtained, showing a repulsive force even at the pole, though it is here a minimum. The scale of these different curves is not given as being unimportant, since it may be changed by varying the velocity $\beta_1 c$ of the negative electron.

Interpretation of the above Theory as applied to the Atom.

It appears at once from (35) that the repulsive force upon a negative electron produced by the vibration of the positive charge in the manner described may be large even when compared with the electrostatic forces which normally hold the electrons in close association with it. For, provided β_2 is great enough to render the bracket negative, that is in excess of $\sqrt{2}/2 = 0.707$, the force is repulsion and its value depends upon the factor $(1-\beta_1^2)^{-\frac{1}{2}}$ in the coefficient, which

approaches infinity as the translational speed of the negative electron approaches the velocity of light. But the mass of the electron itself also approaches an infinite value in a similar manner and by the same form of function, for we have the well-known relation

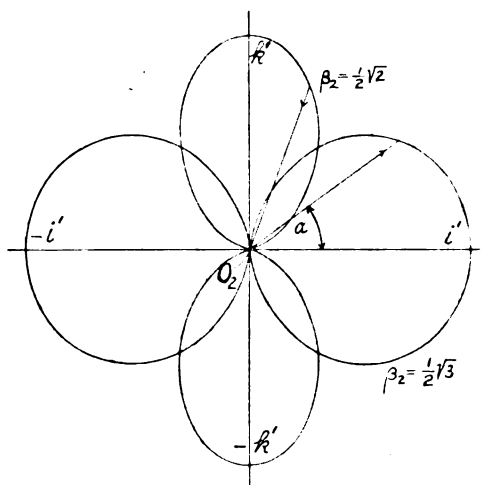
$$m = \frac{m_0}{(1 - \beta_1^2)^{\frac{1}{2}}}, \quad \dots \quad (41)$$

where m and m_0 are the masses at velocities $\beta_1 c$ and zero respectively.

Neglecting the reactive force due to the radiation from the electron in translational motion at present, and equating the whole force in (35) to the mass times the acceleration, the factor $(1 - \beta_1^2)^{-\frac{1}{2}}$ cancels out, giving

$$\frac{d^2 r}{dt^2} = \frac{F}{m} = \frac{F(1 - \beta_1^2)^{\frac{1}{2}}}{m_0} = \frac{e^2}{kr^2 m_0} \left[-1 + \frac{2(1 - \beta_2^2)}{(1 - \beta_2^2 \sin^2 \alpha)^{\frac{1}{2}}} \right]. \quad \dots \quad (42)$$

Fig. 9.



Representing the same as fig. 8, but for two critical values of β_2 , namely $\frac{1}{2}\sqrt{2}$ and $\frac{1}{2}\sqrt{3}$.

The above discussion, illustrated by the curves in figs. 7, 8, and 9, shows the important role that is played by the direction of the axis of the positive charge, represented in the formula by the angle α , for it is clear that this axis is free to be turned in response to the forces acting upon it

even during the brief interval when the electron has been temporarily separated from the positive charge. In the curve of fig. 8 corresponding to $\beta_2=0.8$, for example, there is a critical angle α_0 at about $60^\circ 10'$ where the force changes sign from repulsion to attraction as the axis turns through this angle from a smaller to a greater value.

In this equation, (35) or (42), it is to be supposed that not only does the angle α vary with the time as the electron at O_1 (fig. 5) moves away from the atom, but that r , β_1 and β_2 are each functions of the time. It does not seem possible without further help to make valid assumptions as to these variables as functions of the time.

Some light upon the question is afforded by a consideration of the energy relations. Regarding the hydrogen ion at O_2 (fig. 5) as a single physical system, let us apply to it the ordinary rules of dynamics. Since the entropy of any material system left to itself is known to tend toward a maximum, this may be interpreted here to mean that the ion strives to be rid of its energy at a maximum rate. Now the kinetic energy of translational motion of the electron at O_1 is a part of the energy originally possessed by the positive charge of the ion. If the ion succeeds in driving this electron free completely away from itself carrying with it this kinetic energy, then its own energy will be reduced at a far greater rate than it would be if it depended merely upon the energy lost by radiation.

For, as will be shown later, the kinetic energy at some points of its path is much greater than the total energy radiated by the whole motion. To render the entropy a maximum, therefore, the ion strives to get rid of an electron. As shown above, there exists a certain critical angle α which reduces the whole force to zero, and if the ion could immediately turn itself to this angle, the force would remain zero and the translational velocity of the electron would then become constant because it would retain its original velocity of projection. No energy would be radiated out into space by this uniform velocity and zero acceleration, for the rate of radiation is zero for uniform motion, but the condition for maximum entropy would be fulfilled.

The legitimate inference from this reasoning is that the forces governing the direction of the axis of the positive charge strive to make it assume this critical angle, α_0 , as soon as possible. But in so doing the mass of the ion, or its angular momentum, requires that a certain amount of time be consumed in this operation, causing the axis first to be carried beyond the critical angle and then to be

reversed in its motion, thus oscillating about the angle α_0 with a damped motion. The damping must be present because the value of β_2 is continually decreasing owing to loss of energy by radiation from the electron into space.

The maximum value of the periodic force must, according to fig. 8, be greater the greater the maximum departure from the critical angle, α_0 , during a complete period. But the amplitude of this motion must be a function of its frequency, and it seems most logical to assume that the greater the frequency the smaller the amplitude of the motion. This may mean that the maximum force varies on this account alone as the inverse of the frequency.

The force according to (35) is also inversely as the square of the distance r , but r itself will be a periodic function of the time, and it is shown below that the maximum values of r vary inversely as the frequency. These two causes operating together, therefore, make the maximum values of the periodic force vary directly as the frequency of oscillation of the pole of the positive charge. This matter is stressed because it is unusual to find a force in mechanical systems whose maximum values vary as the frequency, but the above model points to this condition.

With the above understanding it seems entirely justifiable to assume that the acceleration expressed by (42) may be written as a simple periodic function of the time as follows :

$$\frac{d^2r}{dt^2} = k_1 \omega e^{-\omega t} \cos \omega t, \quad . \quad . \quad . \quad (43)$$

where ω is the angular velocity corresponding to a frequency, ν , such that $\omega = 2\pi\nu$. The presence of the factor ω in the coefficient makes the maximum values of the force, as above stated, directly proportional to the frequency ν , k_1 being a constant to be determined. The presence of a damping factor, $e^{-\omega t}$ has been accounted for by the loss of energy due to radiation from the electron moving with accelerated motion.

Granting that this is the typical form that the acceleration expressed by (42) would take, were it possible to deduce it as a function of the time alone, the velocity may be found by a first integration with respect to the time, giving

$$\frac{dr}{dt} = \frac{1}{2} k_1 e^{-\omega t} (\sin \omega t - \cos \omega t) + k_2, \quad . \quad . \quad . \quad (44)$$

k_2 being the constant of integration. When the time is infinite it may be assumed that the electron has returned to resume its original position in the atom, and that $dr/dt = 0$. Hence $k_2 = 0$, and no constant is required. A

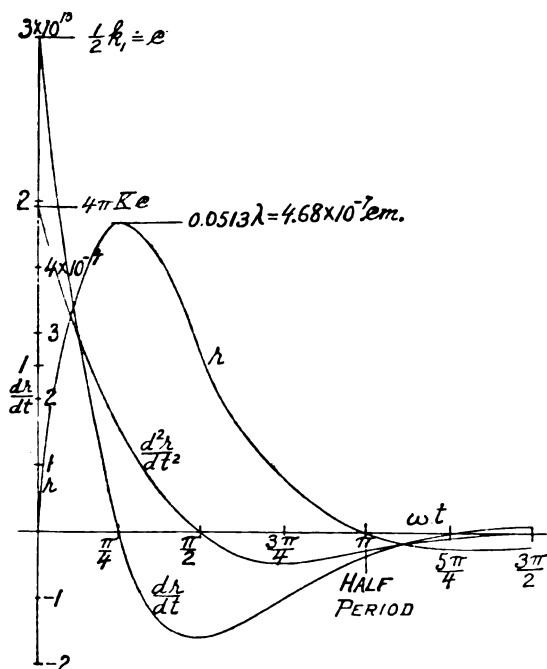
second integration gives the distance r , as follows :

$$r = -\frac{1}{2} \frac{k_1}{\omega} e^{-\omega t} \sin \omega t + k_3, \quad . \quad . \quad . \quad (45)$$

k_3 being a second constant of integration. This is also negligible because when the time is infinite $r_\infty = k_3$, and the distance from the centre of the atom to the normal centre of the electron in the atom is of the order of 10^{-13} cm. and quite negligible.

This expression for r shows that the maximum values vary inversely as the frequency other things being equal, which confirms the statement made above in regard to the distance r that occurs as r^{-2} in the expression for the force.

Fig. 10.



Three curves representing the acceleration, velocity, and distance respectively of the electron at O_1 (fig. 5), moving along the line joining it with the hydrogen ion at O_2 plotted as a function of the time. The maximum separation from the ion occurs at $\omega t = \pi/4$ and is equal to 0.0513 of the wave-length of the radiated wave. The total energy radiated is equal to one quantum, $h\nu$.

Three curves marked $\frac{d^2r}{dt^2}$, $\frac{dr}{dt}$, and r in fig. 10 represent the equations (43), (44), and (45) for certain assumed numerical

values of the constants. $k_1/2$ according to (44) is equal to the initial velocity of projection of the electron from the atom. The frequency ν is assumed for these curves to be equal to the Rydberg constant 3.29×10^{15} as representing the maximum frequency in the spectrum of hydrogen. The angles ωt are the abscis-æ in each of the three curves.

The maximum distance of the electron from the ion is reached when $\omega t = \pi/4$, one eighth of a cycle, at which time the velocity is zero and reverses direction. Putting $\omega t = \pi/4$ in (45) and giving the initial velocity $k_1/2$ its maximum possible value, approximately the velocity of light, c , the maximum distance the electron is driven from the ion is given by

$$r_{\max.} = \frac{c}{\omega} e^{-\pi/4} \sin \frac{\pi}{4} = \frac{c}{\omega} \times 0.456 \times 0.707 = 0.322 \frac{c}{\omega}. \quad (46)$$

Now $\omega = 2\pi\nu$, and $\lambda\nu = c$, we have

$$r_{\max.} = 0.0513 \lambda, \quad \dots \dots \dots (47)$$

where λ is the wave-length of the radiated waves.

Further reference will be made to this result in a subsequent section.

The Total Energy Radiated during One Excursion of the Electron.

An expression for the rate of radiation of energy when a point charge moves in a curved path has been obtained by Liénard and has been shown by Schott* to agree with his deductions, both of these authors using the same form of electrodynamics, that of Larmor and Lorentz. Its expression is as follows:—

$$\dot{R} = \frac{2}{3} c e^2 \left[\frac{\beta^4}{\rho^2 (1 - \beta^2)^2} + \frac{1}{c^4} \frac{(d^2 r / dt^2)^2}{(1 - \beta^2)^3} \right], \quad \dots \dots (48)$$

where ρ is the radius of curvature of the path, $\frac{d^2 r}{dt^2}$ the acceleration along the path, and β its velocity in terms of that of light, c .

The force on the electron caused by the reaction of the

* 'Electromagnetic Radiation.'

radiation in the direction of the tangent to its path follows from the definition of $\dot{R}$, since

$$\dot{R} = \frac{dE}{dt} = F \frac{dr}{dt} = Fr = F\beta c, \quad . . . \quad (49)$$

with due regard to the sign according to whether the reaction of the radiation or a force equal and opposite to it is meant. Schott has given examples computing the total energy radiated when the motion is circular (*loc. cit.* p. 110), simple harmonic motion in a straight line (p. 122), and elliptical motion (p. 126), and shows that his results are obtainable from (48) above.

Since we have previously expressed and supported the view that the Larmor-Lorentz form of electrodynamics is in error in certain respects, and have shown that the Saha form of the theory removes these objections, it would be preferable now to use Saha's expression for the rate of radiation, were it known to the writer, instead of that of Liénard in (48). There seems scarcely any doubt that the form in (48) is defective or at the least incomplete when the case of simple harmonic motion in a straight line alone is considered. At the middle point of the motion the velocity is a maximum and the acceleration zero, hence at this point by (48) $\dot{R}$ is zero as in uniform motion, and by (49), since dr/dt is not zero, F is zero, and there is no reaction due to radiation which is as it should be. As however, the point approaches the end of its harmonic path the velocity dr/dt approaches zero, and the acceleration approaches a maximum. Hence by (48) $\dot{R}$ is a maximum toward the end of the path, but by (49) the reactive force equal to $\dot{R}/v$ approaches infinity as close as we please, since v approaches zero as near as we please, while $\dot{R}$ has its maximum value.

Physically this is unthinkable that the reactive force should approach so large a value in any part of the path, even though no difficulty is apparent when the total energy per cycle is computed. It is also realized that it is generally admitted that this formula only applies to an actual charge, an electron, which has a finite volume, provided the radius of curvature of its path is large as compared with the dimensions of the charge, but this restriction is hardly sufficient to remove the objections to the formula.

The fact that the expressions for the ponderomotive forces of a second moving point charge upon a first differ

so greatly as between the Lorentz and the Saha electrodynamics makes it quite certain that the Saha expression for the rate of radiation when obtained will differ materially from (48), but some interest may attach to the use of (48) in the meanwhile before the Saha expression is available. For straight line motion ρ is infinite and (48) becomes

$$\dot{R} = \frac{2e^2}{3kc^3} \left(\frac{d^2r}{dt^2} \right)^2 \cdot \cdot \cdot \cdot \cdot \quad (50)$$

The dielectric constant k is here inserted in order to keep the dimensions of both members of the equation the same. It should also have been written in (48), but that stands as quoted from the original author.

Assuming that the motion of the electron at O_1 (fig. 5) is completely described by the equations (43), (44), and (45) and illustrated by fig. 10, the total energy radiated during one whole excursion may be obtained from (50) by integration with respect to the time between the limits zero and infinity. Writing for β in (50) $\frac{1}{c} \frac{dr}{dt}$ we have the total energy

$$E = \int_0^\infty \dot{R} dt = \frac{2e^2}{3kc^3} \int_0^\infty \left[1 - \frac{1}{c^2} \left(\frac{dr}{dt} \right)^2 \right]^{-2} \left(\frac{d^2r}{dt^2} \right)^2 dt, \quad (51)$$

or, expanding into series, this becomes

$$E = \frac{2e^2}{3kc^3} \int_0^\infty \left[1 + \frac{3}{c^2} \left(\frac{dr}{dt} \right)^2 + \frac{6}{c^4} \left(\frac{dr}{dt} \right)^4 + \frac{10}{c^6} \left(\frac{dr}{dt} \right)^6 + \dots \right] \left(\frac{d^2r}{dt^2} \right)^2 dt. \quad (52)$$

Using the values of the acceleration and velocity given in (43) and (44) above and integrating each term separately gives finally for the total energy radiated in one excursion of the electron out and back

$$E = \frac{\pi e^2 k_1^2}{2kc^3} \left[1 + \frac{23}{90} \left(\frac{k_1}{c} \right)^2 + \dots \right] \nu. \quad (53)$$

The next term of this series will be k_1^4/c^4 with a different numerical coefficient, and so on, the powers of k_1/c increasing by 2 from term to term. But k_1 is constant by hypothesis according to (43), and there exist, therefore, no variables in the right member of (53) except the frequency of the

exist in hydrogen is $h\nu = hK = 0.2154 \times 10^{-10}$ erg, which is but the two hundred and twentieth part of the kinetic energy just computed, and this kinetic energy is much less than that at some other points.

The importance of the above conceptions, if true, is so great that some of the more fundamental points may bear restating. An initial velocity closely approaching that of light may be produced in an electron which is shot out in a straight line to a limited distance and then returns again to the atom. The energy thus lost by radiation from the atom is no greater than that received from the passing electron from which the energy was originally received. Because the form of this energy received from the passing electron is entirely transformed in character into high-frequency vibrations of the positive charge, the whole internal energy of the positive charge becomes available energy for the time being, and some of this great store of internal energy is used to give the ejected electron its large kinetic energy of translational motion, but this is all returned again to the atom. The positive charge undoubtedly contains a store of energy, $mc^2 = 1.49 \times 10^{-3}$ erg, which is very great compared with any of the other energies mentioned. Hence it becomes possible for a very much smaller amount of energy, that of the passing electron, to release a much larger amount of energy, namely some of that stored within the positive charge. This may be called the trigger effect. Although such an effect has been mentioned in the literature as a remote possibility, I am not aware that its probability from the standpoint of electrodynamics has ever been pointed out. To admit of its existence will be shown in a subsequent communication to remove the usual difficulties connected with the photoelectric effect and secondary β -rays generated by X-rays. These are the two chief phenomena that seem to demand the artificial conception of "light quanta," which of itself introduces difficulties far more formidable than to admit of a trigger effect.

The Law of Force upon an Electron.

According to the above results the force acting upon the electron at precisely the same distance from the ion on its outward journey is very different from the force upon it at this distance on the return journey. The reason for this is clear, that the ion has changed its character in the meantime. The law of force according to this must not only be a function of the distance but of the time also. Attempts

have been made by various authors in the past to deduce a law of force as a function of the distance from experimental observations, but their results have been discordant. The laws found for one case do not work well for other cases and changed conditions. These discordant results are quite in agreement with the conception above mentioned that there is no such thing as a law of force dependent upon the distance only. The time must also enter into these functions.

The Absolute Values of the Maximum Distances to which an Electron is Projected from Hydrogen.

According to (47) the maximum distance to which an electron goes from the atom is proportional to the wave-length of the radiated waves, λ . The shortest wave-length of the hydrogen spectrum is 911.78×10^{-8} cm., corresponding to the frequency $K = 3.28880 \times 10^{15}$, the Rydberg constant. Hence in this case the distance given by (47) is 4.677×10^{-7} cm. If the hydrogen gas in the vacuum tube is at 0° C. and the pressure is one millimetre of mercury, the approximate distance between the molecules of the gas on the average is about 65.5×10^{-7} cm., or about fourteen times greater than the maximum distance computed above. On the average, therefore, the ejected electron will not come within the sphere of influence of the next molecule of the gas, and will experience no disturbance or interference from this cause.

As the frequency of the characteristic radiation is reduced and the wave-length increased the maximum distance becomes greater. The wave-length must be increased fourteen times in order that the electron may go on the average as far as the next molecule. This would make the wave-length about $12,760 \times 10^{-8}$ cm., which is not far from the second line of the Paschen series in the infra-red, so that practically the whole of the observed spectrum of hydrogen may be emitted before an electron travels so far as the next adjacent molecule on the average, and no interference will thus be experienced.

Concluding Remarks.

The complex nature of the behaviour of the atom contemplated in this paper has seemed to require a presentation less abbreviated than is customary in order that the meaning intended may be made clear. The phenomena that have been described are of a fundamental nature, and have a

wide application in every phase of atomic action. It is believed that the conceptions of a high-frequency vibration of the elementary charges themselves, regarded as quasi-solid bodies, and of radiated energy taking place in quanta because an electron is temporarily shot out from an atom and in most cases returns to it again, will prove fruitful in clearing up many phenomena now obscure.

The radiation emanating from these ejected electrons, which falls upon an atom in the eye or in a photographic plate exposed to it, can be shown by means of the ponderomotive force equation (1) to exert a force upon the positive charge of such atoms having the same periodicity as that belonging to the ejected electrons by virtue of their accelerated motion (43). It is almost axiomatic, not requiring any detailed proof, that this frequency or period is transmitted through without alteration and makes itself felt upon the receiver.

The question as to how the line spectrum of hydrogen or any other element may be produced has not been treated because it would extend the paper to undue length, but the derivation of the frequency equation of the line spectrum of hydrogen may be obtained in a manner analogous to that suggested by Whittaker* in 1911. He then attributed the spectrum to the gyroscopic connexion between the two atoms of the hydrogen molecule, and deduced the equation of the Balmer series on this basis. Instead of the gyroscopic connexion being between the two atoms of the molecule it is between the electron ejected from the atom and the remainder of the atom itself, that is the ion, for it is now quite certain that the atom rather than the molecule is the source of these spectra.

In closing it may be emphasized that the treatment in this and the three preceding papers points to the probability that the total energy content of the elementary positive and negative charges is of the utmost importance, as being the key to most atomic actions, because it is drawn upon temporarily in radiation, in the dissociation of the atoms of a molecule, that is all chemical reactions, and probably in all phenomena. Its value, mc^2 , is so great by comparison with all observed cases of energy transfer that temporary changes in it escape observation.

In a subsequent communication it is hoped to show how the ideas above presented throw light upon other phenomena not mentioned here.

* E. T. Whittaker, Proc. Roy. Soc. ser. A, vol. lxxxv. No. A 578, p. 262, June 9, 1911.

III. *On the Theory of Ionization by Swiftly Moving Electrified Particles and the Production of Characteristic X-Rays.* By SVEIN ROSSELAND *.

INTRODUCTION.

A COLLISION between an electrified particle and an atom will in general not conform to the laws of classical dynamics. The deviations from these laws become especially apparent when considering electrons moving with small velocities in inert gases or metallic vapours. In this case, as was first shown by Franck and Hertz, the electron will lose no energy at all if the velocity is below a certain critical value, while there is a considerable probability that it will lose all its energy in a single collision if this value is exceeded. As is well known, this effect is in accordance with the quantum theory of atomic structure. In fact, when a slowly moving electron collides with an atom in the normal state, we may on the basis of Bohr's theory expect that if the electron loses energy in the collision this energy must correspond to the transference of the atom to some other stationary state, and in experiments it is found that the critical velocity just corresponds to the transference of the atom from the normal to the next stationary state †. On the other hand, if the velocity of the incident particle is large compared with the velocities of the electrons in the atom, it is to be expected that the effect of a collision may be calculated with great approximation on the basis of the classical system of mechanics. A strong support for this view is, among other things, provided by the theory of ionization produced by swiftly moving electrified particles. In this paper we shall consider some aspects of this theory and its bearing on the production of characteristic X-rays.

I. IONIZATION BY IMPACT OF α AND β PARTICLES.

§1. *General Theory.*

A theory of the ionization produced by α and β rays was first proposed by J. J. Thomson ‡. In this theory the electrons are considered as being initially at rest and the mutual action between the incident particle and each of

* Communicated by Prof. N. Bohr.

† Compare J. Franck and G. Hertz, *Physikalische Zeitschrift*, xx. p. 132 (1919).

‡ J. J. Thomson, *Phil. Mag.* xxviii. p. 449 (1912).

Phil. Mag. S. 6. Vol. 45. No. 265. Jan. 1923.

the electrons is calculated as if the electron were uninfluenced by interatomic forces, supposing the interaction between the particle and an electron to conform to the law of the inverse square. It is easily calculated that the energy Q transferred to an electron in a collision of this kind is

$$Q = \frac{2m_1m_2^2}{(m_1+m_2)^2} V^2 \sin^2 \frac{\theta}{2}; \quad \tan \frac{\theta}{2} = \frac{eE}{V^2} \frac{m_1+m_2}{pm_1m_2}. \quad (1)$$

where m_1 , $-e$, m_2 , E are the mass and charge of the electron and the particle respectively, while p is the least distance from the initial position of the electron to the path of the particle before the collision; θ is the angle of deflexion of the particle in its motion relative to the common centre of gravity. Putting $Q=W$ the energy necessary to remove the electron from the atom and denoting the corresponding p by p_W , we obtain

$$p_W^2 = \frac{2e^2E^2}{m_1V^2} \left(\frac{1}{W} - \frac{(m_1+m_2)^2}{2m_1m_2^2V^2} \right). \quad (2)$$

In the following p_W will be termed "the radius of ionization." The number of collisions per unit path experienced by the particle with the electrons of a particular group of the atom, in which the energy transferred to the electron is larger than W , is $\pi p_W^2 Nn$, where N is the number of atoms per unit volume and n the number of electrons in the group. Thus the total number of electrons removed from the group by the incident particle per unit path is

$$I = \frac{2\pi e^2E^2Nn}{m_1V^2} \left(\frac{1}{W} - \frac{(m_1+m_2)^2}{2m_1m_2^2V^2} \right). \quad (3)$$

This expression was by Thomson taken to be equal to the number of pairs of ions produced by the particle per unit path. As observed by Thomson, this formula gives a close representation of the relative number of ions produced by α and β particles, as well as the dependence of the ionization upon the velocity of the particle.

The total number of pairs of ions produced by α rays from RaC in air per unit path was determined by Geiger*. From the measurements of Taylor on the relative ionization produced by α rays in air and hydrogen, Bohr† calculated that the absolute number of ions produced by an α particle per cm. at the initial part of its range was several times larger than that predicted by (3). This excess effect was

* H. Geiger, Proc. Roy. Soc. A, lxxxii. p. 486 (1909).

† N. Bohr, Phil. Mag. xxx. p. 606 (1915).

attributed to the secondary ionization produced by the electrons expelled from the atoms. As the velocity of these electrons will be considerably smaller than that of the primary particles, the ionization produced by these electrons cannot be calculated on the simple assumption underlying formula (3), as the problem in reality is one of quantum dynamics. Using some simplifying assumptions Bohr deduced a formula giving an upper limit for the secondary ionization to be expected, and showed that this formula predicted the right order of magnitude of the ionization produced by α rays in hydrogen and helium. This result is of great interest, as it indicates, as presupposed, that for high velocities of the incident particles, and for violent collisions resulting in the removal of an electron from the atom, calculations based on the classical dynamical laws will give also the absolute value of the primary ionization.

When the velocity of the particle becomes of the same order of magnitude as that of some electrons in the atom with which it collides, formula (3) loses all claim of validity, inasmuch as the assumption that the electrons are initially at rest is not even approximately fulfilled, while at the same time the experiments of Franck and Hertz show that it is precisely in this region that the peculiar deviations from the laws of ordinary mechanics become apparent. It will also be found that the formula of Thomson does not even approximately correspond to experiment in this region; but it is after all interesting to note that it predicts a qualitatively right result, as is seen upon comparing it with the measurements of Kossel* and Mayer† of the ionization produced in gases by slowly moving electrons, as well as by α rays. The point is that both theory as well as experiment demand that the ionization shall increase initially to a sharp maximum and next decrease more slowly as the velocity of the particles is further increased. The exact position of the maximum is extremely difficult to determine experimentally, but it is found to occur when the velocity of the incident particles is a few times larger than that of the electrons in the atom. The ionization curve given by Thomson's formula rises much more rapidly to a maximal value than the experimental curves. Considering the experimental difficulties associated with the determination of the elementary ionization on this part of the curve, this disagreement is probably not larger than might be expected already on the

* W. Kossel, *Ann. d. Phys.* xxxvii. p. 393 (1912).

† F. Mayer, *Ann. d. Phys.* xlv. p. 1 (1914).

basis of the classical system of mechanics, when we remember that the electrons in the atom are revolving with velocities which on this part of the curve are of the same order of magnitude as the velocity of the incident particles.

§ 2. Multivalent ions produced by a single impact.

Consider a particle penetrating through an atom of some substance. Around the path of the particle as an axis, supposed to be a straight line, imagine a cylindrical surface with a radius equal to the radius of ionization of a definite electronic group. Suppose, for simplicity, the electrons of the group independently distributed on the surface of a spherical shell with radius r . Let σ denote the ratio of the part of the spherical surface situated within the cylinder to the area of the whole sphere.

The probability that out of the n electrons of the group a number m shall at a time be situated within σ is then

$$P = \frac{n! \sigma^m}{m! (n-m)!} (1-\sigma)^{n-m}. \quad (4)$$

Let q be the distance from the centre of the group to the axis of the cylinder. The mean number of collisions per unit path in which q lies between q and $q+dq$ is $2\pi N q dq$, where N is the number of atoms per cm. The number of m multiple ions produced is accordingly

$$I_m = \frac{2\pi N n!}{m! (n-m)!} \int_0^{r+p_w} \sigma^m (1-\sigma)^{n-m} q dq. \quad (5)$$

Let us fix our attention on the case in which the electronic group contains two electrons, corresponding to the neutral helium atom or the K-group of the other elements. The exact value of I_m even in this case is seen to be very complicated. We shall therefore be satisfied with approximate expressions. When p is small compared with r , the ratio σ will be small and we may approximately put

$$\sigma = \frac{1}{4\pi r^2} \frac{2\pi p_w^2}{\sqrt{1 - \frac{q^2}{r^2}}} = \frac{p_w^2}{2r^2} \frac{1}{\sqrt{1 - \frac{q^2}{r^2}}}, \quad (6)$$

and take the limits of the integral to be 0 and $r-p_w$. The

number of doubles is

$$I_2 = -\frac{\pi}{4} N \frac{p_2^4}{r^2} \log_n \left(\frac{2p_2}{r} - \frac{p_2^2}{r^2} \right) \quad . \quad . \quad . \quad (7)$$

and of singles

$$I_1 = 2\pi N p_1^2 \left\{ 1 + \frac{p_1^2}{4r^2} \log_n \left(\frac{2p_1}{r} - \frac{p_1^2}{r^2} \right) \right\} \quad . \quad . \quad (8)$$

From the experiments of Franck and Knipping* it is known that the ionization potential of helium, when both electrons are removed at one time, is more than double of the ionization potential of one electron. The values of p in the formulæ (9) and (10) are therefore marked with different indices. The percentage of doubles is approximately

$$\epsilon = \frac{1}{8} \frac{p_2^4}{p_1^2 r^2} \log_n \left(\frac{2p_2}{r} - \frac{p_2^2}{r^2} \right) \quad . \quad . \quad . \quad (9)$$

When, on the other hand, p_2 is larger than r we may put $\sigma = 1$ for $q < p - r$ and $\sigma = \frac{1}{2} \left(1 + \frac{p - q}{r} \right)$ when $p - r < q < p + r$.

The number of doubles, singles, and percentage of doubles are found by an easy calculation to be

$$I_2 = \pi N [p_2^2 + \frac{1}{3}r^2 - \frac{5}{6}p_2r] ; \quad I_1 = \frac{4}{3}\pi N p_1 r ;$$

$$\epsilon = \frac{p_2^2 + \frac{1}{3}r^2 - \frac{5}{6}p_2r}{p_2^2 + \frac{1}{3}r^2 + (\frac{4}{3}p_1 - \frac{5}{6}p_2)r} \quad . \quad . \quad . \quad (10)$$

In the region where p and r are of the same order of magnitude neither (9) nor (10) will apply. However, drawing a diagram by means of these formulæ for large and small values of p/r , the probable course of the curve for moderate values of p/r will be given within narrow limits by an interpolation as shown in fig. 1, used in the next section.

§ 3. Dimensions of the Helium atom.

The preceding calculations are capable of direct application to the experiments of Millikan† and Wilkins‡ on the production of divalent ions in helium. It was found that the percentage of divalent ions varied roughly in the same manner with range as the total ionization in the ordinary Bragg curve, and increased from about 8 per cent. at the

* J. Franck and P. Knipping, *Phys. Zeitschr.* xx. p. 7 (1919).

† R. Millikan, *Phys. Rev.* xviii. p. 456 (1921).

‡ T. R. Wilkins, *Phys. Rev.* xix. p. 210 (1922).

middle of the range of the alpha particle to about 16 per cent. at the top of the ionization curve, after which the percentage decreased rapidly to zero. As the only unknown quantity in the above expressions is r , these experiments will yield a value for the radius of the helium atom.

In order to calculate the radius r from the experiments we must first calculate the values of p_1 and p_2 . Limiting ourselves to a region where Thomson's formula may be considered to be valid, we first notice that the ratio p_1^2/p_2^2 is nearly equal to the ratio P_2/P_1 , where P_1 , P_2 are the ionization potentials for one electron of helium, according as one electron or both are removed from the atom in one collision. From the work of F. Horton and A. C. Davies* and J. Franck and Knipping† it is known that P_1 is close to 25.4 volts. When this value is taken for granted the value of P_2 is unambiguously given by Bohr's theory as $\frac{1}{2}(4.13 \cdot 5 + 25.4) = 39.8$ volts. In fact, the experimental value given by Franck and Knipping is in complete accord with this value.

We now calculate the percentage of double catches for small and large values of p_1/r by means of the formulæ (9) and (10) and interpolate for intermediate values. Knowing the radius r , the absolute values of the percentage may be obtained by introducing the values of p_1 and p_2 calculated from Thomson's formula at a part of the range where this formula may be assumed to be valid. However, we shall prefer by reversing the argument to calculate the radius r and compare the result with the values given by the kinetic theory of gases and the quantum theory.

The velocity of the alpha particles from polonium is $V = 1.55 \cdot 10^9$ cm. sec.⁻¹. At the middle of the range it has decreased to $V = 1.25 \cdot 10^9$ cm. sec.⁻¹. From the observed value of the ionization potential we then calculate the corresponding p_1 to be $2.93 \cdot 10^{-9}$ cm. Millikan‡ states that at the middle of the range the percentage of doubles is about 8 per cent. From the curve (fig. 1) the corresponding ratio p_1/r is seen to be close to 1.25. By means of the calculated value of p_1 , this gives $r = 2.5 \cdot 10^{-9}$ cm. This value is four times smaller than the value afforded by the kinetic theory of gases (ca. 10^{-8} cm.)§, but it will be seen to be of the same order of magnitude as that predicted by Bohr's theory. If the two electrons revolve in circular one-quantum orbits,

* F. Horton and A. C. Davies, Proc. Roy. Soc. xcv. p. 408 (1919).

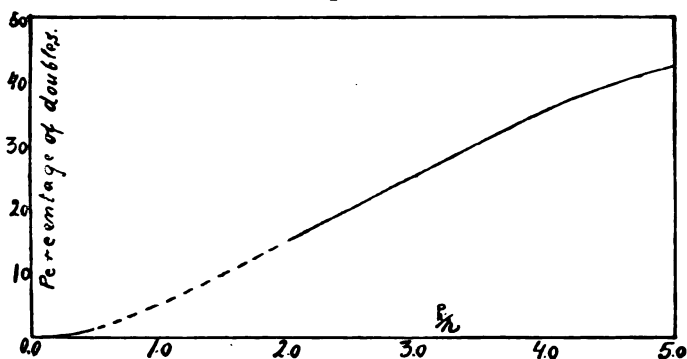
† J. Franck and Knipping, Phys. Zs. xx. p. 5 (1919).

‡ R. Millikan, Phys. Rev. xviii. p. 458 (1921)

§ Jeans, 'Dynamical Theory of Gases,' sec. ed. p. 341.

the radius of the orbits will on this theory be close to 3.10^{-9} cm.* This figure will be only little affected, whether we assume the orbits to be coplanar or inclined to each other. Conversely, assuming the value of r to be that given by the quantum theory, the percentage of doubles at the middle of the range comes out about 5 per cent. This value differs from that given by Millikan by scarcely more than the experimental error. These calculations thus seem strongly to suggest that the dimensions of the electronic orbits in the helium atom really are as small as demanded by Bohr's theory. Experiments of this kind seem to be of special interest, since we are here more directly concerned with the

Fig. 1.



dimensions of the electronic orbits, and need not take account of the complicated phenomena associated with a collision between two neutral atoms.

Our calculations are of course to some extent affected by the special distribution of electrons assumed. For the most unfavourable case when the two electrons constantly are placed at the opposite ends of a diameter through the nucleus, the probability of double ionization is easily seen to be of the order

$$\epsilon = \frac{1}{16} \frac{p_2^4}{p_1^2 r^2}, \quad \dots \dots \dots (11)$$

if p_2 is not larger than r . For the present case the percentage of doubles predicted by this expression will be about half as large as that predicted by the combination of (9) and (10). Although this result at present hardly permits of drawing any definite conclusions, it indicates that accurate

* N. Bohr, Phil. Mag. xxvi. p. 476 (1913).

experiments of this kind may be of value for an investigation of the configuration of the electrons within the group of the helium atom. The possible bearing of these experiments on the electronic configurations in helium was pointed out by Millikan *, but it is to be emphasized that his arguments are not conclusive without fixing the value of the atomic dimensions, and especially that no conclusion of this kind can so far be drawn from the observations near the optimal ionization. In fact, in this place the velocity of the α particles has become of the same order of magnitude as the velocity of the electrons in the atom. The motions of the two electrons during a collision cannot then be treated separately, and it is not certain that differences in the initial motion of the two electrons of the kind considered by Millikan will have any sensible influence on the probability of double catches.

II. INTENSITIES OF CHARACTERISTIC X-RAYS.

§ 1. *Production of X-ray spectra on the quantum theory.*

According to Bohr's theory of atomic structure † the electrons in an atom in the normal state are divided into groups in such a way that the orbits of the electrons in each group are characterized by a principal quantum number, the value of which is equal to one for the innermost group and increases by one unit when we pass from group to group in the direction from the nucleus outwards.

When a high speed electron is projected through the atom electrons may be ejected from the different groups. The rest of the atom reorganizes provisionally into a stationary state, in which, however, the number of electrons in the different groups is now different from that corresponding to the most stable arrangement of the remaining electrons. The atom reorganizes ultimately into a final stable state through a series of successive processes of transition, during each of which an electron is transferred from an outer to an inner group characterized by a smaller principal quantum number. Each of these processes is accompanied by the emission of a train of harmonic waves of frequency ν given by the relation $h\nu = E' - E''$, where E' and E'' are the values of the energy of the atom in the initial and the final states.

The intensities of the characteristic X-rays will primarily depend upon two circumstances. Firstly upon the number

* R. Millikan, *Phys. Rev.* xviii. p. 459 (1921).

† See for instance N. Bohr, *Zs. für Phys.* ix. p. 1 (1922).

N_i of atoms in the anticathode in a particular stationary state i prepared for X-ray emission; and secondly upon the probabilities A_k^i of spontaneous transition* from the given stationary state i with a given distribution of the electrons in the different groups, to another stationary state k with the same total number of electrons in the atom, but where one electron has been transferred from an outer to an inner group. If ν_{ik} is the frequency of the radiation emitted by a transition between the stationary states i and k , the energy emitted in the form of radiation of this frequency in the time interval dt from the atoms of the anticathode is

$$dI = N_i A_k^i h \nu_{ik} dt. \quad . \quad . \quad . \quad (12)$$

In this expression the A_k^i are constants of the atomic configurations, which, on account of the fundamental assumptions underlying the quantum theory in its application to atomic structure, are necessarily independent of the manner in which the stationary state in question is brought about, i. e., in the case of the excitation of characteristic X-rays, independent of the voltage applied to the X-ray tube.

Whatever function N_i may be of the voltage applied to the X-ray tube, the form of expression (14) involves an immediate conclusion concerning the relative intensities of all X-ray lines emitted when atoms in a specified stationary state i suffer spontaneous transitions into a series of stationary states k . For since N_i is the same for all these lines, the relative intensities of these lines will depend only upon the different products $A_k^i \cdot \nu_{ik}$, and thus will be independent of the voltage applied to the tube. This conclusion is generally confirmed by experiment.

In the general case N_i signifies the number of atoms with an arbitrary number of electrons absent from the different electronic groups. From the actually observed X-ray spectra it is seen that the majority of the lines are emitted from atoms that have lost but a single electron from the inner groups. However, as pointed out by Wentzel†, a number of satellites appearing in the lightest elements, which hitherto have escaped classification, may be explained by assuming that they are emitted by atoms that have lost two or more electrons from the inner groups. But since the intensities of these lines are small compared with that of the principal lines of the spectrum, and as they preferentially appear in the spectra of light elements, we shall in the

* A. Einstein, *Physikalische Zeitschrift*, 1917, p. 122.

† G. Wentzel, *Ann. d. Phys.* lxxi. p. 437 (1921).

discussion of the dependence of intensity of the characteristic X-rays upon voltage provisionally neglect the distinction between single and multiple ionization.

§ 2. *Dependence of intensity of X-ray lines upon the voltage applied to the X-ray tube.*

Consider an electron moving an element of path dx in the anticathode. During the motion it will collide with the atoms lying close to the path and lose energy to the electrons of the atoms. By far the greater part of the loss of energy will be due to collisions with the numerous loosely bound electrons belonging to the outer groups of the atoms. But there will also be a number of collisions with the strongly bound electrons of the inner groups. Let $I(E)$ be the number of collisions with electrons of some inner group experienced per unit path by an electron moving with a kinetic energy E , in which these electrons are actually ejected from the atom. The total number of electrons removed from the group in question is then obtained by integrating $I dx$ along the path of the particle until the energy of the particle is just equal to the energy of ionization of the group in question. The mean decrease of energy per unit path of a swiftly moving electron is known from theory as well as from experiments to be of the form *

$$\frac{dE}{dx} = k \cdot \frac{N}{\frac{m}{2} \cdot V^2}, \quad \dots \dots \dots (13)$$

where k is a function of E increasing slowly with decreasing E , but which for the present purpose may be treated as a constant. V is the velocity of the electron and E is for all velocities given by the relativity formula

$$E = mc^2 \left(\sqrt{1 - \frac{V^2}{c^2}} - 1 \right)$$

where c is the velocity of light.

For voltages of the same order of magnitude as W the path travelled in the anticathode will be so small that it is unlikely that the absorption of the X-rays in the anticathode will influence the intensity of the emitted radiation to any appreciable extent. Similarly, the scattering of the electrons within the anticathode is immaterial in this connexion as

* See the discussion by Bohr, Phil. Mag. xxx. p. 594 (1915).

long as we can neglect the effect of the absorption of the emitted radiation in the anticathode. From experiments, however, the scattering is known to be so large that an appreciable number of electrons is actually reflected from the target. The velocities of these electrons have been measured and found to be essentially smaller than that of the incident electrons. For our purpose all electrons moving with a kinetic energy smaller than the ionization energy W_i are of no consequence. This circumstance is of essential importance, and we must expect to obtain results of the right order of magnitude when neglecting the fraction of the incident particles reflected with an energy greater than W_i . The number of electrons thrown out from the electronic group considered per unit time is

$$ze \int I(E) dx. \quad . \quad . \quad . \quad (14)$$

where ze is the current passing through the tube. Introducing E as an independent variable from (12), we obtain

$$N_i = \frac{ze}{k \sum_s A_s^i} \int_{W_i}^{E_0} I(E) \frac{1}{2} m V^2 dE. \quad (15)$$

where $\sum_s A_s^i$ is the total probability of spontaneous transition from the state i . From (15) we obtain

$$I(E) = \frac{k N \sum_s A_s^i}{\frac{1}{2} m V^2} z \frac{\partial N_i}{\partial E}. \quad . \quad . \quad . \quad (16)$$

The intensity of a certain X-ray line corresponding to the state of ionization characterized with the letter i is

$$F_i = A_{ik}^i h \nu_{ik} N_i. \quad . \quad . \quad . \quad (17)$$

We may therefore write

$$I(E) = \frac{k N}{a_{ik} z h \nu_{ik}} \frac{1}{\frac{1}{2} m V^2} \frac{\partial F_i}{\partial E}. \quad . \quad . \quad . \quad (18)$$

where $a_{ik} = \frac{A_{ik}^i}{\sum_s A_s^i}$ is the relative probability of spontaneous transition from the state i to the state k .

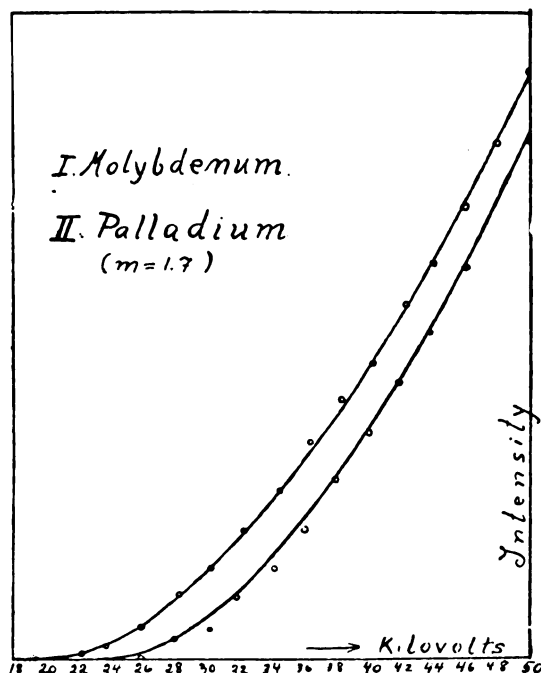
By means of this equation we can deduce $I(E)$ from the experimental voltage-intensity curves, as long as E is not so large compared with W_i that the absorption in the anticathode of the excited radiation must be taken into account.

Experimental voltage-intensity curves have been obtained by D. Webster* for the K_α and K_β lines of rhodium, by

* D. Webster, *Phys. Rev.* vii. p. 599 (1916).

Webster and Clark * in the case of the L_α -lines of platinum, and by B. A. Wooten † in the case of the K_α and K_β lines of molybdenum and palladium. These curves can be represented by functions of the form $I = \text{const} (E - W)^m$, where m lies between $3/2$ and 2 , as is shown in fig. 2 for the experiments of Wooten. The corresponding functions $I(E)$

Fig. 2.



are then of the form $I(E) = \text{const.} \frac{(E - W)^{m-1}}{V^2}$. For the present case the variability of the mass of the electron with speed will not make any essential difference. Putting $\frac{1}{2}mV^2 = E$ we find that $I(E)$ will increase rapidly to a maximal value at $E = \frac{W}{2-m}$, after which it decreases with increasing E . This is a characteristic feature exhibited by all ordinary ionization curves. However, the experimental material presently at hand covers so small a range of

* Webster and Clark, Proc. Nat. Acad. Sc. iii. p. 181 (1917).

† B. A. Wooten, Phys. Rev. xviii. p. 71 (1919).

voltage that even the existence of a maximum in $I(E)$ cannot be inferred with certainty. It would therefore be very interesting to have the experiments extended to other elements and to a wider range of voltage covering also the gradual falling off of the ionization behind the maximum value.

In the main the function $I(E)$ may, apart from a difference of linear scale, be expected to exhibit the same qualitative properties independent of the element and the X-ray lines which have been employed in the experiment. In detail, however, differences may occur, as for instance in the relative height and position of the maximal point. For values of E which are large compared with the ionization energy of the electron in the group in question $I(E)$ may be expected to be given by the simple expression (3). The expression $I(E)$ may in general be considered to be the product of the number n of electrons, contained in the group in question, and an individual ionization function which principally will depend upon the energy of the incident particle and the ionization potential of the electron in question, and only to a minor extent on the special kind of the interaction with the other electrons in the group. It might therefore be expected, that experiments of this kind will afford a direct manner of determining the number of electrons in the different electronic groups of the atom.

On the whole, experiments on characteristic X-ray intensity seem to offer a method of studying the process of ionization under various conditions. This method seems to possess several advantages, since each X-ray line is associated with the primary ionization of a definite electronic group, while in ordinary experiments on ionization in gases we have, apart from hydrogen and helium, to do with more complex phenomena. The experiments can further be extended to a much wider range of ionization potentials, and finally the part of the ionization curve accessible by this method is just the part which offers the greatest experimental difficulties in the case of experiments on ionization in gases.

§ 3. *Efficiency in producing characteristic X-rays.*

As we do not know the absolute value of the ionization performed by electrons in inner atomic groups, we cannot calculate the absolute value of the intensities of X-ray lines. An upper limit for the intensity should be expected to be

obtained by introducing $I(E)$ from formula (3) in (15) and (16). Neglecting the relativity modifications we obtain

$$F = \frac{n\pi e^4}{k} \left\{ \frac{E_0 - W}{W} - \log \frac{E_0}{W} \right\} \sum_k a_{ik} \dot{h} \nu_{ik}. \quad (19)$$

In the experiments referred to above the absolute value of the intensity is in no case recorded. An estimate of the ratio of the intensity of the X-ray lines to that of the continuous radiation in the case of molybdenum and palladium can be obtained from the measurements of Clayton Ulrey *. From Ulrey's diagrams it appears that this ratio for the characteristic K-lines is about 1/2 for Mo and 1/4 for Pd. The voltage applied was 35,000 volts.

The efficiency in producing general radiation can be calculated from the formula

$$\eta = 2.7 \cdot 10^{-10} AV, \quad V = \text{voltage, } A = \text{atomic weight.} \quad (20)$$

which is shown by Beatty † and Rutherford and Barnes ‡ to hold for a wide range of voltages and for a large number of elements. The constant factor corresponds to that found by Rutherford and Barnes §. Proceeding in this way we find for the efficiency in producing characteristic X-rays in Ulrey's experiments, $6.5 \cdot 10^{-4}$ and $3.5 \cdot 10^{-4}$ for molybdenum and palladium respectively.

From formula (19) we can calculate an upper limit for the efficiency F/Ez . The sum $\sum_k a_{ik} \dot{h} \nu_{ik}$ will be of the order of W_i , while k can be interpolated from Whiddington's || experiments on the decrease of velocity of cathode rays in Al and Au. The value adopted is $k = 3 \cdot 10^{-35} \text{ gr.}^2 \text{ sec.}^{-4}$ for both Mo and Pa. With the values of the critical potentials found by Wooten and Ulrey the efficiency calculated from (21) is about $12 \cdot 10^{-4}$ and $6 \cdot 10^{-4}$ for Mo and Pa respectively, when assuming $n=2$ for the K-group. These values are twice as large as those deduced from experiment, but the difference is probably not larger than was to be expected from the nature of the calculation, and the large experimental errors involved in the determination of the efficiency of producing general X-radiation as well as in the determination of the stopping power of the different elements for cathode rays.

* C. Ulrey, *Phys. Rev.* xi. p. 401 (1918).

† Beatty, *Proc. Roy. Soc.* lxxxix. p. 314 (1913).

‡ Rutherford and Barnes, *Phil. Mag.* xxx. p. 361 (1915).

§ Compare also Rutherford and Barnes, *L. c.* p. 367, footnote.

|| Whiddington, *Proc. Roy. Soc.* lxxxvi. p. 360 (1912).

§ 4. *Enhanced lines in X-ray spectra.*

As mentioned above, Wentzel has pointed out that some X-ray lines which do not fit in the ordinary scheme of classification can be explained on the assumption that they are emitted by atoms which have lost more than one electron from an inner group. Wentzel supposes that this double ionization of the atom is due to successive impact. On account of the probably very short life-period of the excited state of an inner electronic group, this assumption can hardly be maintained. It will appear that the multiple ionization in question can to a measurable extent only be due to simultaneous action by a single impacting particle.

Consider the probability of successive collisions in the simple case when an ionized atom having lost a single electron from an inner group loses a second electron from the same group before reorganization of the atom has taken place. The probability that the ionized atom in question in the time dt will experience collisions with impacting particles resulting in a second ionization of the same group is

$$dF = n\pi p_W^2 \frac{s}{e} dt, \quad . \quad . \quad . \quad (21)$$

where n is the number of electrons in the group considered, s the current density of impacting particles, and p_W the radius of ionization. The probability that the atom in the time dt will suffer a spontaneous transition from the state considered under emission of radiation is $A dt$, where A is a constant. The ratio of the number of doubly ionized atoms to the number of singles is

$$\tau = \frac{\pi n p_W^2 s}{A e} . \quad . \quad . \quad . \quad (22)$$

This ratio will be seen to be vanishingly small for all cases when electrons are removed from inner groups of the atom where the probability of spontaneous transition is conditioned only by the state of the atom itself. Considerations based upon the principle of correspondence indicate that A ought to be of the order $10^8 \cdot Z^4$, where Z is the effective nuclear charge of the group. On the other hand, p_W^2 will be of the order $10^{-16} Z^{-4}$. For a current density of 1 ampere s/e is of the order 10^{19} , and consequently it is seen that τ is very small in all cases involving the ionization of inner groups. Similar considerations apply also when the collisions do not result in the removal of an electron from an inner group,

but only in a transference of an outer electron from its normal orbit to an orbit characterized with a quantum number some units higher. This problem has been discussed by Compton*. As the life period of these states must increase rapidly with increasing quantum number, the part played by successive collisions will also increase rapidly, until when complete ionization of an outer group is obtained it may under favourable conditions play a preponderant part. While thus successive impact may be the essential cause of the multiple ionization responsible for the appearance of the optical spark spectra, we must assume that the multiple ionization giving rise to enhanced lines in X-ray spectra must be due to simultaneous action by a single impact.

The double ionization performed by α particles in helium has been shown to be intimately connected with the dimensions of the electronic orbits and the number of electrons in the helium atom. In the same manner the intensities of enhanced lines in the X-ray spectra are directly connected with the dimensions of each electronic group and the number of electrons contained in it. As no systematic measurements of this kind have been performed, we shall be content with showing in broad outlines that the experimental material at hand is consistent with the assumption that the multiple ionization is due to single impacts.

Assume for simplicity, as before, that the electrons are independently distributed on the surface of spherical shells. This special form of the distribution will not seriously influence the result, as an alternative assumption of uniform volume distribution within a sphere will lead to practically the same dependence upon r and p apart from a slowly varying factor. Consider the general case when an incident electron removes m_1 electrons from a group containing n_1 electrons . . . and m_s electrons from a group containing n_s electrons. Using the same notation as in § 2, section 1., we obtain in analogy to the formulæ (4) and (5) for the probability of a particular arrangement of the electrons when s groups are concerned,

$$P = \prod_{i=1}^{i=s} \frac{n_i! \sigma_i^{m_i}}{m_i! (n_i - m_i)!} (1 - \sigma_i)^{n_i - m_i}, \quad \dots \quad (23)$$

* Compton, *Phys. Review*, xv. (2) pp. 130 and 476 (1920). A significant exception occurs when the state in question is of the metastable kind, where A is equal to zero. In this case successive collisions with other atoms of the gas or with the impacting particles will necessarily occur. The importance of this point is mentioned by J. Franck, *Phys. Zs.* xxii. p. 443 (1921).

and for the number of collisions of the type in question experienced per unit path by the incident electron

$$I_m = 2\pi N \int P q dq, \quad (24)$$

where the integration is to be extended to all values of P different from zero. The expression for the intensity of a particular line with frequency ν_{ik} will be of the form

$$F_m = \frac{a_{ik} h \nu_{ik}}{k N} \int_{W_c}^{E_0} I_m E dE. \quad (25)$$

As before, a_{ik} is the relative probability of the transition giving rise to the line in question, and W_c is the critical potential of the line. This potential will be different from the critical potential of the corresponding line, which is due to single ionization, and roughly equal to the sum of the potentials necessary to remove each electron separately from the neutral atom. According to (24) the intensity of enhanced X-ray lines will be expected to increase according to a law different from that which is valid for ordinary lines.

Consider for the sake of illustration the simple case of double ionization of the K-group. As the ratio $\frac{p}{r}$ in the case of elements with higher atomic numbers will be small, we can use the simple expression for I_2 given by (9) and neglect $\frac{p_2^2}{r^2}$ in the logarithmic term as well as the distinction between p_1 and p_2 . Introducing further p^2 from (2) we thus obtain

$$F_2 = a_{ik} i \frac{h \nu_{ik}}{k} \frac{\pi}{8} \frac{e^8}{r^2 W^2} \int_{W_c}^{E_0} \log_n \left(\frac{r^2 E^2 W}{4 e^4 (E - W)} \right) \times \frac{(E - W)^2}{E^3} dE. \quad . . . (26)$$

The critical potential W_c is approximately equal to $2W$.

The relative intensity of an enhanced line to the corresponding line due to single ionization is seen, by using the expressions (19) and (26) for a constant ratio E_0/W , to be sensibly inversely proportional to $(2rW)^2$, which in this case will again be nearly equal to $Z^2 e^4$. The enhanced X-ray lines in the K-series due to double ionization of the K-group may thus be expected to decrease rapidly with increasing atomic number of the element.

A similar conclusion will hold for the relative intensities of the other enhanced lines in the K- as well as in the other series, which, as may be inferred from (24), will decrease

Phil. Mag. Ser. 6. Vol. 45. No. 265. Jan. 1923. G

with increasing Z . Further, as may be seen from (22), the relative intensities will decrease with increasing value of s .

These considerations are in accordance with experimental facts. First, the strongest enhanced lines observed correspond to double or triple ionization, and the lines which are due to double ionization are stronger than those due to triple ionization. Secondly, the intensity of enhanced lines decreases rapidly with increasing atomic number, so that in the K-series these lines have not been observed systematically for elements with atomic number higher than 30. It is further shown in a paper by Coster * which has just appeared, that the intensity of some lines in the L-series, which probably belong to the enhanced lines, increases in a different way with increasing voltage from the ordinary L-series lines and in a manner which qualitatively conforms to (26), although the measurements did not give an accurate measurement of the critical potential. This is of great interest in this connexion, and measurements especially on the critical voltage of the ordinary enhanced lines will afford a crucial test of this theory and a reliable means of disentangling the lines due to multiple ionization from those due to single ionization.

In the K-series in the elements from sodium to zinc one of the strongest enhanced lines observed is K_{α_1} , which corresponds to a transition of an L-electron into the doubly ionized K-level. Accurate measurements on the intensity of this line compared with that of the principal K_{α} lines for different voltages may, as seen from equation (25) or (26), offer direct test of the theoretical values for the dimensions of the K-group. In the same manner measurements on the intensity of the enhanced line L_{α_3} in the L-series may yield information about the dimensions of the L-group, and so on. It is, however, to be remembered that lines resulting from different processes of ionization may have the same frequency. Consider thus the line K_{α_1} , which appears when an electron from the singly ionized L-group passes into the singly ionized K-group. The state in which one electron is missing from the K-group and one from the L-group can, however, either be produced directly by a collision or indirectly from a state in which both K-electrons are removed.

In the same paper Wentzel, in support of his assumption that the enhanced X-ray lines were due to collisions by successive impact, refers to the complex structure of the absorption edges, observed by Fricke, Hertz, and Stenström,

* D. Coster, *Phil. Mag.* xliv. p. 546 (1922).

which he explains as due to absorption of atoms having already lost an electron by a previous process of absorption. This assumption, however, can scarcely provide the right explanation of the phenomenon. The relative intensity of the different "components" of an absorption edge must, namely, on this hypothesis be expected to be nearly equal to the ratio of the number of atoms with electrons absent from some inner group to the total number of neutral atoms in the material used in the experiment; but under the ordinary experimental condition this ratio will probably be far too small to yield any satisfactory explanation. The problem is examined in detail in the above-mentioned paper by Coster, where also a different explanation of the complex structure of the absorption edges is discussed.

Summary.

The theory of ionization by swiftly moving electrical particles is discussed in its relation (1) to the experiments of Millikan and Wilkins on the production of divalent ions in helium by α -rays, (2) to the increase of intensity of characteristic X-rays with increasing voltage, and (3) to the occurrence of certain lines in the X-ray series which are due to multiple ionization of the inner electronic groups (enhanced lines).

It is pointed out that the phenomenon of multiple ionization of an atom produced by the action of a single particle is directly connected with the dimensions of the different electronic groups. In this manner the dimensions of the electronic orbits in helium are calculated from Millikan's experiment, and found to be of the order predicted by Bohr's theory. It is also shown that experiments on the dependence of intensity of characteristic X-rays on voltage afford a direct means of investigating the number of electrons in the inner electronic groups of the heavier atoms and the dimensions of these groups. In this connexion the appearance of X-ray lines originating from doubly ionized atoms is discussed, and it is concluded that these lines are excited by a single impact of an electron on the atom and not by successive impacts.

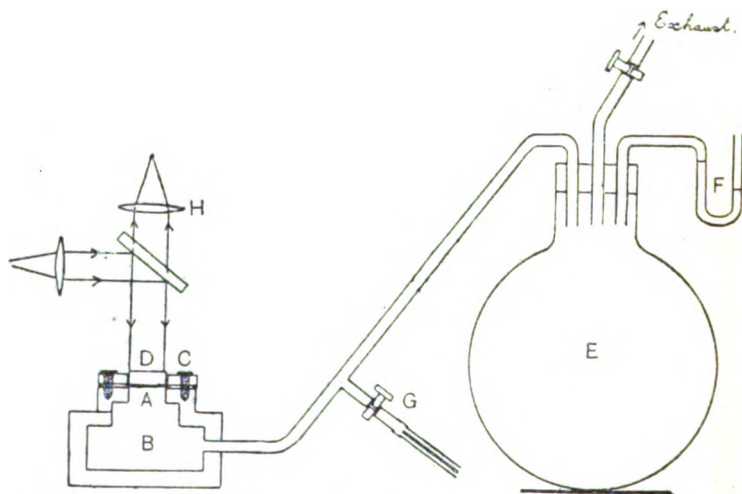
In conclusion I wish to express my best thanks to Prof. N. Bohr for his kind interest and help throughout the work.

Institute of Theoretical Physics,
University of Copenhagen.

IV. *Application of an Optical Manometer to the Measurement of the Viscosity of Gases.* By J. E. P. WAGSTAFF, M.A., *Lecturer in Physics at the University of Leeds* *.

A DELICATE form of optical manometer, recently described in the *Proceedings of the Camb. Phil. Soc.*†, has been used as a pressure-gauge for measurements of the viscosity of air. This method of measuring small changes of pressure has been found to possess considerable advantages over the usual method adopted in this type of experiment of taking two simultaneous readings of a moving mercury column. A thin slip of glass A (diameter 2 cm.), whose modulus of elasticity is known, is made to rest on the top

Fig. 1.



of a pressure-chamber B (*vide* fig. 1), in the upper surface of which is a circular hole of diameter 1.93 cm. In order to clamp the edges of the slip, a brass plate C, having a hole of diameter 1.97 cm. concentric with that in the upper surface of the chamber, is screwed down on the top surface of the glass slip. A small plate of glass D (diameter 1.95 cm. approx. and thickness 1 mm.) is made to rest on the top of the slip, care being taken that the air in the space between

* Communicated by the Author.

† Wagstaff, *Proc. Camb. Phil. Soc.* vol. xx. Part 1.

the slip and the plate remains at atmospheric pressure. The chamber is connected to a reservoir E, which can be partially exhausted by means of a filter pump. Air can be allowed to enter the apparatus very slowly through a fine capillary tube of known dimensions by opening the tap G. The film between A and D is illuminated by a parallel beam of monochromatic light, and is viewed by a microscope at H. The time taken for a given number of circular fringes to close in towards the centre is observed, from which the change in pressure in the chamber E in a given time can be calculated, and the viscosity determined.

Theory. In the case of a gas of viscosity η flowing through a tube of length l cm. and radius a cm., the rate of flow is determined by the equation

$$p_1 v_1 = \frac{\pi a^4 (p_2^2 - p_1^2)}{16 \eta l},$$

where p_1 and p_2 are the pressures of the gas at the two ends of the tube, and v_1 is the volume of the gas flowing through the tube per sec. at pressure p_1 .

If S = combined volume of the vessel E and of the pressure-gauge B, p_2 the pressure of the external atmosphere, and T the time taken for the pressure inside the apparatus to rise from p_1 to p_3 , it has been shown that *

$$\frac{1}{2p_2} \left[\log_e \frac{p_2 + p'}{p_2 - p'} \right]_{p_1}^{p_3} = \frac{\pi a^4 T}{16 \eta S}.$$

Write

$$p_3 = p_1 + p_1',$$

$$\text{then } \log_e \left(1 + \frac{p_1'}{p_1 + p_2} \right) - \log_e \left(1 - \frac{p_1'}{p_2 - p_1} \right) = \frac{\pi a^4 T p_2}{8 \eta l s},$$

where p_1' , corresponding to the disappearance of a given number of fringes for light of wave-length λ , can readily be calculated from the formula

$$p_1' = \frac{256 E t^3 N \lambda}{90 R^4},$$

for a plate of radius R , thickness t , and Young's modulus E , which is clamped at the edge. Several sets of observations were made for various values of p_1 , the initial pressure inside the apparatus, which can be observed quite accurately with a cathetometer; the results are tabulated below.

* Searle, Camb. Phil. Soc. vol. xvii. Part 2, p. 183.

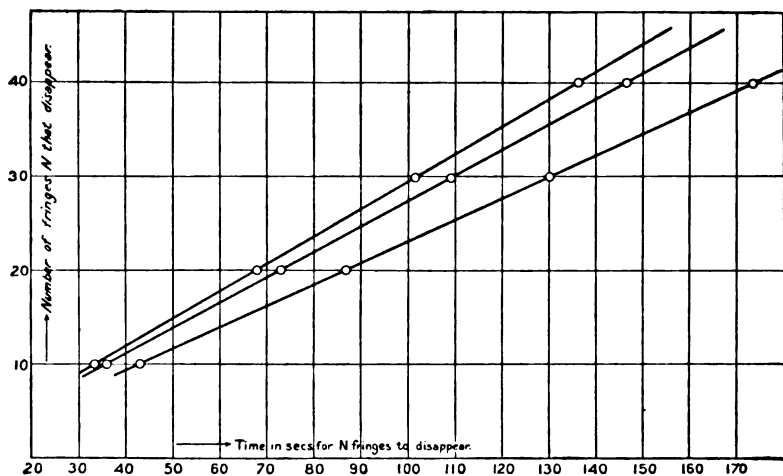
SERIES I.

Length of capillary tube = 61.6 cm.

Barometric pressure = $p_2 = 75.89$ cm.Temperature = $18^\circ.5$ C.

$p_2 - p_1$.	N = number of fringes that disappear.	T = time taken for N fringes to disappear.
24 cm.	10	33.6 sec.
	20	68 "
	30	101.5 "
	40	136.5 "
22.1 cm.	10	36 "
	20	73 "
	30	109.3 "
	40	147 "
18.1 cm.	10	43 "
	20	87 "
	30	130.5 "
	40	173.9 "

Fig. 2.



When N is plotted against T as in fig. 2, a straight line relationship is indicated.

In a second series of experiments, the time taken for a given number of fringes to disappear for different initial pressures is observed ; the results are given below.

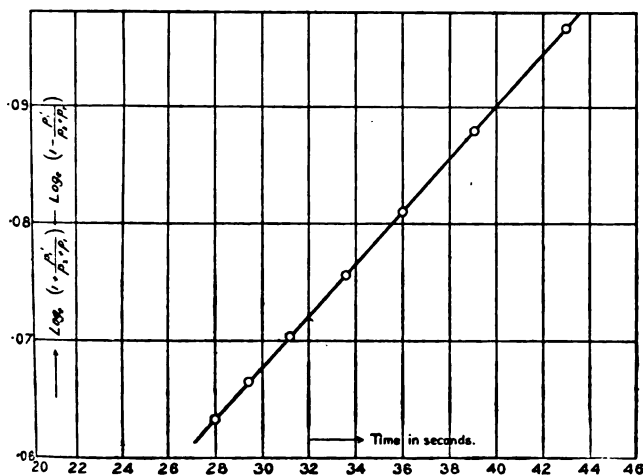
SERIES II.

Volume of reservoir E and chamber B = 4,800 c.c.

$\theta = 18^{\circ}5$ C. $N = 10$.

$p_2 - p_1$ cm. of mercury.	Time taken for 10 fringes to disappear.	$p_1' = 149$ N.	$\log_e \left(1 + \frac{p_1'}{p_2 + p_1} \right)$ $-\log_e \left(1 - \frac{p_1'}{p_2 - p_1} \right)$.
30.0	28.0 sec.	1.49	.06310
28.0	29.5 "		.06631
26.1	31.3 "		.07023
24.0	33.6 "		.07565
22.1	36.0 "		.08104
20.1	39.0 "		.08818
18.1	43.0 "		.09670

Fig. 3.



Columns 2 and 4 of the above table have been plotted in fig. 3, and a linear relationship between the quantities is indicated. The best fitting straight line through the observations

gives a mean value for

$$\log_e \left(1 + \frac{p_1'}{p_2 + p_1} \right) - \log_e \left(1 - \frac{p_1'}{p_2 - p_1} \right) = \frac{1}{T}.$$

The radius of the tube is found in the usual way by inserting a thread of mercury and finding its length and mass. The mean value of the viscosity of air, under the conditions of the experiment, is now easily deduced and is found to be 1.811×10^{-4} dyne per cm.² per unit velocity gradient. This is in very close agreement with determinations by other methods.

Finally I wish to thank Mr. A. Hare, B.Sc., for his assistance while carrying out the investigation.

V. *The Shape of the Capillary Curve formed between a Flat Glass Plate and a Uniform Circular Cylinder, and the Accurate Determination of the Surface Tension of Liquids.*
By J. E. P. WAGSTAFF, M.A., Lecturer in Physics at the University of Leeds*.

Introduction.

IN the determination of surface tension by means of a capillary tube, one of the difficulties is the accurate measurement of the diameter of the tube at the point to which the liquid rises. Such measurements are always open to considerable inaccuracy. In the following paper I have attempted to eliminate this source of error by forming the meniscus between a uniform circular cylinder containing liquid, and a plate dipping into the liquid and cutting the cylinder along two generators. The problem then resolves itself into the determination of the diameter of a wide tube (say 5 cm.) and of the width of a plate (say 2 cm.). Moreover, the method permits of a number of observations being made on the same liquid during one experiment, and from these the value of the surface tension can be accurately determined.

Description of Experiment.

A plate and a thin-walled circular cylinder, of uniform section, both of glass, are first carefully cleaned by washing with potassium dichromate and concentrated sulphuric acid,

* Communicated by the Author.

and rinsing with distilled water. The cylinder, containing the plate, is then placed on a levelling-table. The liquid under observation is then introduced into the cylinder and the plate is pressed against the wall of the latter so that its edges are vertical, by means of two small glass rods with rubber tips inserted horizontally between the plate and the opposite wall of the cylinder. This is insured by viewing the plate through a microscope with a vertical travel, making a scale-division in the eyepiece coincide with the edge of the plate, and adjusting the screws attached to the table until the scale-division coincides with the edge at all heights. The measurements are made by means of a travelling microscope having a vertical movement which rests on the bed of a measuring machine capable of horizontal motion.

Theory.

Let the curved surface ABEDCF be a portion of the cylindrical vessel of radius R , and ABCD the glass plate of width $2a$ which intersects the cylinder along the generators AD and BC, and suppose that the bottom of the meniscus of the liquid confined between the plate and the cylinder assumes the shape QSPR as indicated in fig. 1. Take a system of rectangular axes at a point O, the intersection of the line GH joining the mid points of AB and CD with the level of the surface of the liquid in the outer vessel, such that OY lies along HG, and OX is in the plane of the plate. Supposing the principal radii of curvature at $P(x_1, y_1)$ are R_1 and R_2 , R_2 being parallel to the plane of the plate, the difference of pressure p between the two sides of the meniscus is given by

$$p = y_1 \rho g = T \left(\frac{1}{R_1} + \frac{1}{R_2} \right),$$

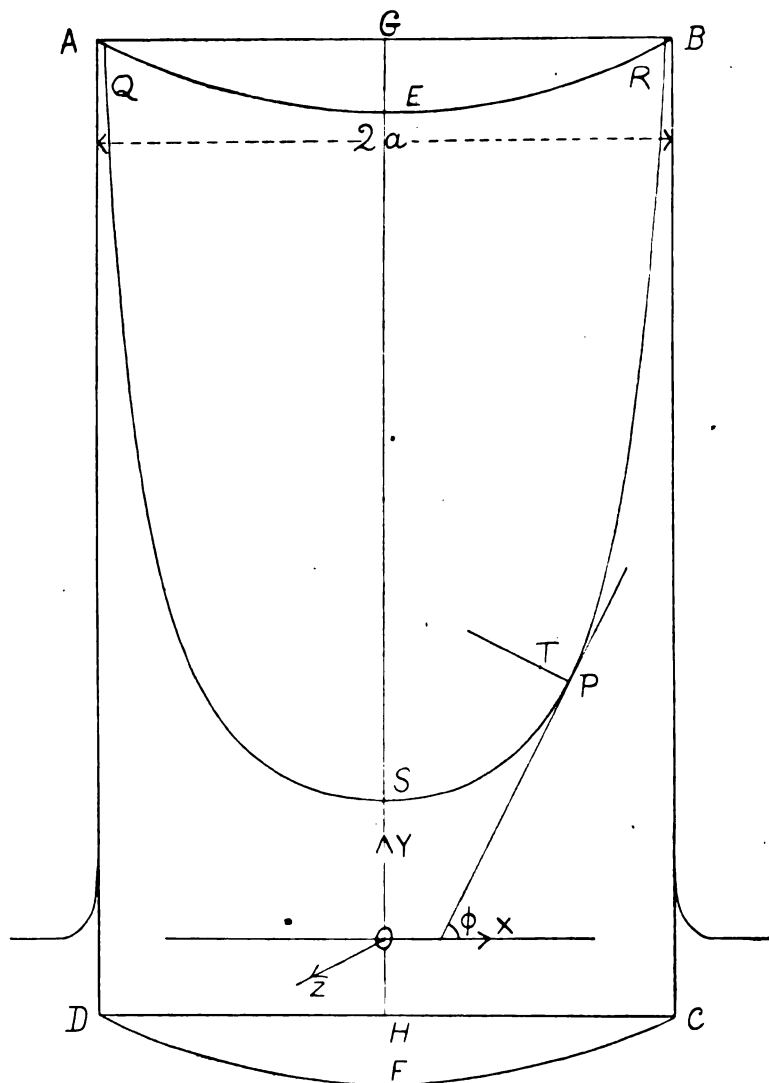
for a liquid of density ρ and surface tension T . Neglecting $\frac{1}{R_2}$ in comparison with $\frac{1}{R_1}$,

$$y_1 \rho g = \frac{T}{R_1}.$$

The equation of the normal to the meniscus at P is

$$y - y_1 = - \frac{x - x_1}{\tan \phi},$$

Fig. 1.



and the distance from P of any point T(x, y) on this line is

$$TP^2 = (x_1 - x)^2 + (y_1 - y)^2 = \frac{(x_1 - x)^2}{\sin^2 \phi} \dots (I.)$$

Let z_0 be the distance between the two glass surfaces at S, and z the corresponding distance at T, then

$$(z_0 - z)(2R - z_0 + z) = x^2, \quad \dots \quad (II.)$$

$$\text{and} \quad z_0(2R - z_0) = a^2. \quad \dots \quad (III.)$$

Moreover, if TP is the depth of the section of the surface of the meniscus at P, by a plane through TP drawn perpendicular to the plane of the figure,

$$TP = R_1(1 - \sin \psi) \quad \text{and} \quad z = 2R_1 \cos \psi,$$

where ψ is the angle of contact between glass and the liquid. In the case of water and glass $\psi = 0$.

$$\text{Thus} \quad (z_0 - 2R_1)(2R - z_0 + 2R_1) = x^2 \text{ for } \psi = 0,$$

$$\text{and} \quad \frac{T}{R_1} = y_1 \rho g.$$

Substituting for R_1 , and writing $\frac{2T}{\rho g} = K$,

$$\left(z_0 - \frac{K}{y_1}\right)\left(2R - z_0 + \frac{K}{y_1}\right) = \left(x_1 - \frac{K \sin \phi}{2y_1}\right)^2.$$

$$\text{Inserting} \quad \frac{K}{z_0} = y_0,$$

$$K\left(\frac{1}{y_0} - \frac{1}{y_1}\right)\left(2R - K\left[\frac{1}{y_0} - \frac{1}{y_1}\right]\right) = \left(x_1 - \frac{K \sin \phi}{2y_1}\right)^2,$$

which is the equation of the projection of the bottom of the meniscus between the two surfaces on the plane $z = 0$. This equation suggests a method of determining T. The quantities

$K\left(\frac{1}{y_0} - \frac{1}{y_1}\right)$ and $\frac{K \sin \phi}{2y_1}$ are small in comparison

with $2R$ and x_1 respectively, so that an approximate value of K will be sufficient to estimate these terms. This approximate value of K is given by

$$K = z_0 y_0,$$

where $z_0(2R - z_0) = a^2$.

The angle ϕ is measured directly from the graph showing x_1 for different values of y_1 (*vide* fig. 2). In practice $2x_1$ is observed at different heights y_1 . If now, in the case of any

92 Mr. Wagstaff: *Shape of Capillary Curve formed*
liquid,

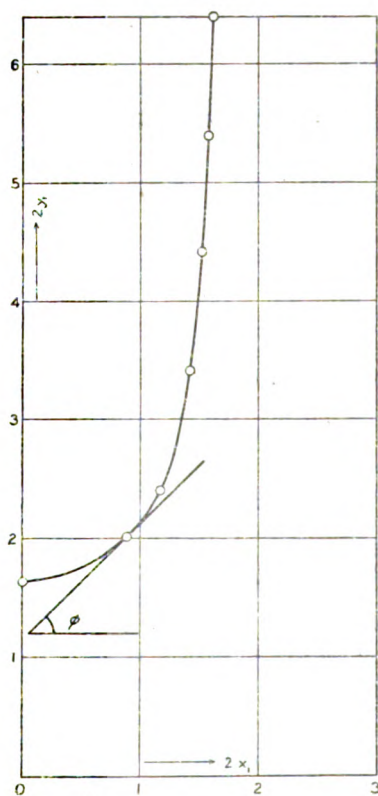
$$\left(\frac{1}{y_0} - \frac{1}{y_1}\right) \left(2R - K \left[\frac{1}{y_0} - \frac{1}{y_1}\right]\right)$$

be plotted against

$$\left(x_1 - \frac{K \sin \phi}{2y_1}\right)^2,$$

the points obtained are found to lie on a straight line as indicated by the theory, and the slope of this line gives the surface tension.

Fig. 2.



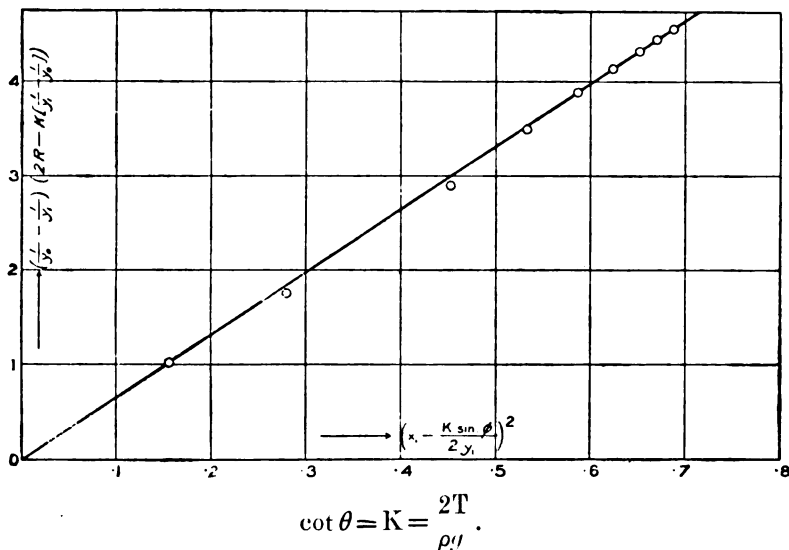
Several sets of observations have been taken for different liquids. Tabulated below are the results obtained with distilled water at 18° C.

TABLE I.
 $2a = 17.6765$ mm. $2R = 4.726$ cm. $y_0 = .825$ cm.
 Approximate value of $K = 1/7$. Temperature of water = 18°C .

$2x_1$ (cm.), x_1 (cm.)	y_1 (cm.)	$y_1 - y_0$, $\frac{y_1 - y_0}{y_1 y_0}$	$2R - K \frac{y_1 - y_0}{y_1 y_0}$	$y_1 - y_0 \left\{ 2R - K \left(\frac{y_1 - y_0}{y_1 y_0} \right) \right\}$	ϕ	$\frac{K \sin \phi}{2y_1}$, $x_1 - \frac{K \sin \phi}{2y_1}$	$\left(x_1 - \frac{K \sin \phi}{2y_1} \right)^2$
0	$y_0 = .825$	0	4.726	0	0	0	0
.87808	.43949	.2171	.03101	1.020	40°	.04568	.1551
1.16563	.58202	.3823	.05461	1.785	67°	.05458	.2790
1.4250	.71295	.6238	.08940	2.902	80°	.04128	.4512
1.6265	.76325	.7586	.10837	3.502	85°	.03227	.5343
1.58498	.79249	.8424	.12034	3.881	87°	.02637	.5869
1.62388	.81194	.9001	.12859	4.137	87.5°	.02226	.6237
1.65108	.82609	.9421	.13459	4.325	88°	.01927	.6507
1.66808	.83404	.9743	.13919	4.470	89.5°	.01699	.6676
1.68613	.84307	.9903	.14276	4.581	89.5°	.01518	.6845
1.69725	.84862	1.020	.14671	4.672	89.5°	.01373	.6972

If θ is the angle of inclination of the straight line drawn through the observations (fig. 3),

Fig. 3.



Hence the surface tension of water at $18^\circ \text{C.} = 74$ dynes per cm.

VI. *A Critical Review of Trouton's Law, and its Applicability at the Triple Point.* By SASI BHUSAN MALI, M.Sc., Research Assistant, University College of Science, Calcutta*.

ACCORDING to the well-known law propounded by Trouton, the ratio of the molecular latent heat of vaporization of a substance to the temperature of vaporization is a constant for all substances, and the value of the constant is approximately equal to 21. It was shown later that the Trouton law is applicable not only in the case of vaporization but also in the case of fusion of substances, the value of the constant being of course different in the latter case. Hence, the generalized Trouton law may be expressed by saying that the latent heat of change of state of a substance

* Communicated by Prof. Megh Nad Saha.

is proportional to the temperature of the change of state, and the ratio of the two is approximately the same for all substances provided the same kind of change of state is involved.

By considering the case of a large number of simple substances, Nernst* has shown that the original Trouton law for vaporization does not hold generally, and he therefore connects the latent heat of vaporization with the temperature of vaporization by an empirical formula of the type

$$\frac{M\lambda}{\theta} = A \log \theta - B\theta,$$

where A and B are constants.

The object of the present paper is to examine critically the validity, and the theoretical foundation, if any, of the Trouton law. It is obvious that the quotient $\frac{M\lambda}{\theta}$ denotes Molecular Change of Entropy during a discontinuous physical change. Thus, if we confine our attention to the phenomena of vaporization, we have

$$\frac{M\lambda}{\theta} = S_1 - S_2,$$

where S_1 = gram-molecular entropy of the vapour phase, and S_2 = gram-molecular entropy of the liquid phase.

The value of the quotient is generally calculated at the boiling-point, *i. e.*, at the temperature at which the substance boils under a pressure of one atmosphere. Now, this particular pressure is a totally artificial point. It has no physical significance such as the triple point, the critical point, or the inversion point has. It varies enormously with the external pressure, while the latent heat varies neither in the same direction nor to the same extent. Thus, let us take the case of water. We calculate the Trouton quotient for water boiling under different pressures.

P.	B.P.	Latent Heat.	Trouton Quotient.
4.6 mm.	0° C.	606.5	40
760 mm.	100° C.	535.9	25.9
20950 mm.	230° C.	446	16

* W. Nernst, *Wärme Satze*, p. 117.

At the critical point the Trouton quotient becomes zero, because the latent heat vanishes there. Thus, the Trouton quotient varies from 0 to 40 as we pass the range downwards from the critical point to the triple point.

An attempt has been made to show that the Trouton quotient may have the same value for all substances, when we calculate it at the corresponding temperatures of these substances. Guldberg* and Guye† tried to show that the boiling-point under atmospheric pressure is two-thirds of the critical point for many substances, which, if true, would afford a theoretical basis for the Trouton law. But unfortunately the relation is very rough as the following table shows.

Substance‡.	Critical point in absolute temp.	Boiling-point in absol. temp.	Quotient.
Ethyl ether	466.8	307.6	0.66
Ethyl alcohol.....	516.1	351.4	0.68
Ammonia	405.53	240	0.59
Argon	152	86.9	0.57
Benzol	561.5	353.2	0.63
Bromine	575.2	331.6	0.58
Hydrobromic acid.....	364.3	204.5	0.56
Chlorine	419	306.7	0.73
Chloroform	531.8	334.2	0.63
Hydrochloric acid.....	324	190	0.59
Carbon dioxide	304	193.8	0.64
Methyl alcohol	513	337.7	0.66
Oxygen	155	90.1	0.58
Sulphuretted hydrogen ...	374.4	213	0.57
Sulphur dioxide.....	430	263	0.61
Nitrogen	126.5	77.33	0.61
Water	647	373	0.58
Hydrogen	32	20.22	0.63

It appeared to the present writer that the Trouton quotient might be found to be constant at the triple point. But calculations which are given below do not support this view. The triple point is only slightly different from the melting-point, therefore the data at the latter point have been used throughout the calculations. We can calculate the latent heat at the melting-point from that at the boiling-point with the aid of these data, making use of Planck's equation

$$\frac{dL}{dT} = (C_{P_1} - C_{P_2}) + \frac{L}{T} - T \frac{dP}{dT} \frac{\delta(V_1 - V_2)}{\delta T}.$$

* Guldberg, *Zeits. Physik. Chem.* v. p. 374 (1890).

† Guye, *Bull. Soc. Chim.* iv. p. 262 (1890).

‡ Landolt and Börnstein, *Tabellen*, pp. 439, 190, and 373.

The last term on the right-hand side is approximately equal to $\frac{L}{T}$ provided we neglect V_2 in comparison with V_1 and apply the perfect gas laws. Then

$$\frac{dL}{dT} = C_{P_1} - C_{P_2},$$

and

$$L_M = L_B - (C_{P_1} - C_{P_2})(T_B - T_M) \text{ approximately,}$$

where

L_M = gram-molecular latent heat at melting-point,
 L_B = gram-molecular latent heat at boiling-point,
 C_{P_1} = gram-molecular specific heat of the vapour phase,
 C_{P_2} = gram-molecular specific heat of the liquid phase,
 T_B = temperature of boiling under one atmosphere,
 T_M = temperature of melting.

The results of calculation for a few simple substances are given in the following table :—

Substance*.	L_B .	C_{P_1} .	C_{P_2} .	T_B .	T_M .	L_M .	$\frac{L_M}{T_M}$.
Nitrogen	1363	6.4	13.3	77° K.	62°·5 K.	1434	23
Hydrogen ...	229	3	4.37	20°·4 K.	14° K.	237.8	17
Argon	1501	3	10.5	87° K.	85° K.	1516	18
Oxygen	1640	7	12.74	90°·1 K.	54°·23 K.	1846	34
Water	...	...	...	...	273° K.	10917	40
Bromine	6960	8.45	16.16	331°·6 K.	265°·68 K.	7462	28

It thus seems to be fairly well-established that there is no particular point of temperature at which the Trouton law holds. Neither does the law seem to have any theoretical significance. The fact that the law approximately holds good for a few selected substances when the vaporization considered is under one atmospheric pressure is of the nature of an accident, rather than of a law.

* Eucken, *Ber. d. Deut. Phys. Ges.* xviii. p. 4 (1916); W. Nernst, *Wärme Satze*, p. 117.

Landolt and Börnstein, *Tabellen*, pp. 185, 750, and 190.

VII. *Cathode Disintegration.* By The Research Staff of the General Electric Company, Ltd., London *.

Summary.

THE disintegration of a tungsten cathode struck by positive ions of various gases at various speeds has been investigated by using as the disintegrated cathode the "grid" of a triode.

(1) The rate of disintegration is independent of the temperature of the cathode.

(2) It increases regularly with the energy of the positive ions and is appreciable when the energy does not exceed greatly that required to ionize the gas. There is no irregularity in the neighbourhood of the normal cathode fall.

(3) It varies with the nature of the gas. The gases investigated could be arranged in the following order of increasing rate of disintegration:—Hydrogen, helium, nitrogen, neon, mercury vapour, argon.

No theory of disintegration is offered at present, for the results are professedly preliminary. But it is suggested that the facts as they stand throw some light upon unsettled problems of the unsupported electric discharge.

Incidentally some observations of the disappearance of the gas in the discharge are recorded; and it is pointed out how well the loss of mass of a wire may be measured by means of its decrease in conductivity.

Conclusions 1, 2, 3 confirm those of a more limited investigation described by Kingdon and Langmuir in a paper published since this work was completed (*Phys. Rev.* vol. xx. p. 107 (1922)).

Introduction.

1. Our knowledge of cathodic disintegration† is based chiefly upon experiments made on the unsupported discharge between cold electrodes. It has been established that with the same cathode in the same gas, the rate of disintegration is proportional to the current and increases with the cathode fall; so long as the cathode fall is "abnormal" the pressure of the gas is important only in so far as it affects

* Communicated by the Director.

† The work published before 1912 is summarized by V. Kohlschütter (*Jahrb. d. Rad. u. Elek.* vol. ix. p. 355 (1912)). References will therefore be only given to work subsequent to that date.

these two factors. In general the loss of mass with the same current and the same cathode fall increases with the molecular weight of the gas and the atomic weight of the metal. The relation between the disintegration and the electrical conditions obviously suggests that the action is due to the impact of positive ions on the cathode and increases with their speed; but since there is as yet no complete theory of the cathode fall, it is impossible to translate in detail information about the effect of change of cathode fall into information about the effect of change of speed. Further, there are certain anomalies shown by the inactive gases; argon and, to a lesser degree, neon are known to be peculiarly active in promoting disintegration when pure, while the disintegration is very greatly reduced if they are mixed with very small traces, less than 1 per cent., of the common gases*; even mercury is effective in reducing the disintegration, although its molecular weight is high. Now the inactive gases have peculiarly low normal cathode fall; it is uncertain whether their peculiarity in causing disintegration is due to a peculiar relation between speed of the ions and the cathode fall, or whether it is really a peculiarity in the disintegration due to ions of a given speed.

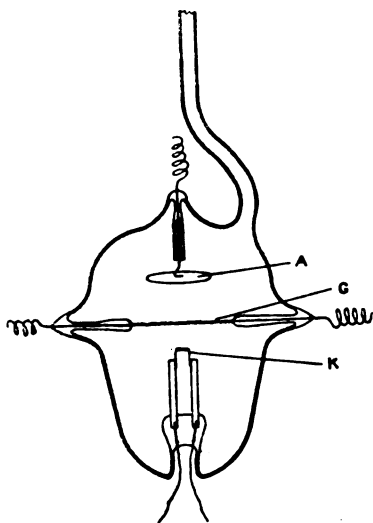
These difficulties in interpretation are made much less serious if a form of discharge is used for which a more complete theory is available. Such a discharge may be obtained in a triode with thermionic cathode. The current to the grid, when the grid is negative to the cathode, is then a measure of the number of positive ions arriving at it, and the speed of the ions arriving is related comparatively simply to the potentials of the electrodes. No experiments on the disintegration of the grid in such a vessel appear to have been undertaken. The measurements described in this paper show that it is a powerful method of investigating disintegration. The results presented here are merely preliminary, but they are sufficient to indicate the scope of the method and to show that the study of disintegration may throw some light on the still unsolved problems of the unsupported discharge. It is because they open up several lines of research in which a knowledge of the laws of disintegration could be used to investigate other problems—lines which we may not be able to follow up ourselves immediately—that we give an account of our experiments in this stage.

* J. Pintsch, Brit. Pat. 155783; D.R.P. Dec. 12, 1917.

Experimental Methods.

2. The discharge vessel employed in these experiments is shown in fig. 1. The cathode K is a tungsten spiral heated by a 6-volt battery, the anode A a nickel plate. (It would doubtless have been better to use a metallic coating on the inside of the bulb as anode, but as many observations had been made before this was realized, the apparatus was not changed.) The grid G is a close spiral of fine tungsten wire, such as is used in gas-filled lamps. The diameter of the wire was $\cdot 05$ mm., of the spiral $\cdot 24$ mm. The vessel was connected through a liquid air trap to a high vacuum pump,

Fig. 1



a McLeod gauge and apparatus for filling and purifying the gases used. A and G were connected to the outside terminals of a potentiometer, between which a potential V_0 was maintained by a battery or generator; K was connected to the movable contact of the potentiometer so that its potential relative to A (V_a) and relative to G (V_g) could be varied.

A microammeter, shunted if necessary, could be inserted alternatively either in the grid or anode circuits, so as to measure the current i_g flowing to the grid, or the current i_a flowing from the anode; i_g was from $0\cdot 2$ to $2\cdot 0 \times 10^{-6}$ amp.; i_a from 15 to 200 times i_g .

3. To determine the loss of mass of the wire its resistance

was measured. This method has often been used before for determining the thinning of a wire*, but it does not seem to have been pointed out how satisfactory it is; it is fairly accurate even if the diameter is not reduced by the same amount at all points along its length. If r is the radius of the wire at distance x from its middle point, ρ the density, σ the specific resistance, l the length, m the mass, R the resistance, and C the conductance, we have

$$m = \int_{-\frac{l}{2}}^{+\frac{l}{2}} \rho \pi r^2 dx; \quad R = \int_{-\frac{l}{2}}^{+\frac{l}{2}} \frac{\sigma}{\pi r^2} dx. \quad (1)$$

If r is constant,

$$mR = m/C = \rho \sigma l^2. \quad (2)$$

If r varies, but varies symmetrically on both sides of the middle (as is the case here and in many other examples), we may write

$$r = r_0(1 + ax^2 + bx^4 + \dots), \quad (3)$$

and, as a first approximation, neglect powers of x higher than the second.

Then

$$\frac{m}{C} = \rho \sigma l^2 \left(1 - \frac{a^2 l^4}{576}\right); \quad (4)$$

so that if the correcting term in (3) for the extreme ends ($x = \frac{l}{2}$) is as great as $\frac{1}{4}$, that in (4) is less than $\frac{1}{500}$.

Accordingly when, as in these experiments, we are dealing with changes in resistance the greatest of which never reaches 25 per cent. of the original resistance of the wire,

we may assume that $\frac{m}{C}$ does not vary by more than 1 per cent., and write with that degree of accuracy

$$dm = m_0/C_0 \cdot dC, \quad (5)$$

where m_0 and C_0 are the original mass and conductivity.

In order to be as free as possible from temperature variations, the grid was balanced in a bridge against a similar spiral in a similar vessel through which no discharge was ever passed. This spiral was taken throughout as the unit of resistance and conductivity; its resistance at 18° C. was about 10 ohms, but it does not need to be known accurately. For if we measure in terms of this standard

* E. g. I. Langmuir, *Phys. Zeit.* xiv. p. 1273 (1913).

the conductivity (C') of various lengths of the wire of which the spirals are made and the corresponding mass m' , we shall find $m'/C' = \text{constant} = \alpha$ (say). Then in (5)

$$m_0/C_0 = \frac{\alpha}{C_0^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and

$$dm = \frac{\alpha}{C_n^2} \cdot dC, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

whereby dm is determined in grams by means of measurements of conductivity in terms of the arbitrary standard. For the wire and the standard used in these experiments, α was .0216 when m is expressed in grams. C_0 was nearly 3. (The standard spiral was about 3 times as long as the grids, being a survival from an earlier type of discharge vessel, which had been abandoned before these experiments were undertaken.) A change in conductivity amounting to 1/1000 part of the standard or 1/3000 part of the grid in its initial condition could be detected; this corresponds to a loss of weight of about .0024 mgm. The method is therefore sensitive as well as accurate.

Owing to the residual changes of conductivity with temperature which were not completely eliminated, the possible error in an estimation of the loss of mass increased with the duration of the experiment and with the consequent chance of change of temperature. An apparent decrease in conductivity of 1 in 1000 occurring during an experiment lasting an hour might be due to change of room temperature; the shortest possible experiment lasted 20 minutes, which was the time that the vessel took to cool after being heated by the discharge. Accordingly there was a limit to the rate of disintegration which could be measured with accuracy, and the estimates of very slow rates, such as those characteristic of hydrogen, were unreliable. The values given for hydrogen or helium may possibly be in error by as much as 50 per cent.; but since this source of error is absolute and not relative, the probable error of this nature with the remaining gases is not more than 2 or 3 per cent. It will be seen in the curves given below that the points vary from the mean line by a far greater amount than this. This variation is not mere experimental error in making the measurements; the larger discrepancies are due to some real variation in the rate of sputtering, the cause of which is not yet completely understood.

The limit of accuracy of the conductivity measurements is set by the heating of the grid and standard by the measuring

current: when the discharge vessel is evacuated, a heating current of 1 ma. changes the resistance by 2 or 3 parts in a thousand. While the grid and standard are of the same diameter this effect is largely compensated, but after disintegration has proceeded for some time the compensation becomes imperfect. Another source of error lies in the leads which, in the arrangement adopted, had a resistance of about 1 per cent. of the standard. Since these various sources of error would have made the absolute values of the loss of mass uncertain to 5 per cent., and since none of the conclusions drawn depend upon absolute values, the work of reduction has been reduced by assuming C_0 the same for all grids. The absolute values of the loss may thus be in error by as much as 20 per cent., but the relative values in different experiments are correct to within 1 or 2 per cent.

4. As might be expected, all observations showed that, when the nature and pressure of the gas, the condition of the grid, and the potentials between the electrodes were unchanged, the loss of mass was proportional to the total quantity of electricity carried to the grid, *i. e.* $\int_T i_g dt$, where T is the time of the discharge. It is therefore convenient to express the disintegration as loss of mass per coulomb of grid current. An even more convenient method of expression is by number of atoms of tungsten lost per positive ion striking the grid. The disintegration S expressed in this manner is given by

$$S = \frac{e}{m_W} \cdot \int i_g dt, \quad (8)$$

where m_W is the mass of the tungsten atom (at. wt. 184) and e the charge of an ion. Therefore

$$S = 523 \frac{dm}{\int i_g dt} \cdot (9)$$

But one source of uncertainty should be noticed. It is here assumed that all the current i_g is carried by positive ions; the current carried by the electrons liberated by the impact of the positive ions is neglected. Experiments are not available to estimate the fraction of the currents carried by these electrons, but there is good evidence that it is a small fraction. Cheney * found that the ratio of the electron to the positive ion current for a platinum cathode struck by Li, K, or Rb atoms with energies corresponding to a few

* W. L. Cheney, Phys. Rev. x. p. 335 (1917).

hundred volts never exceeded 0.1. The fraction apparently increased as the atomic weight of the metal struck decreased, but, since for Al it was only about twice that for Pt, it would not be much greater for W than for Pt. If the fraction were independent of the nature of the positive ions and of their energy, the only effect of the secondary electron emission would be to make the apparent value of S smaller than the real value in a constant ratio; but as this condition is not fulfilled, the relative values of S estimated from (9) may be somewhat in error. However, it seems legitimate to conclude that this source of error will not invalidate such conclusions, mainly qualitative, as are to be drawn here.

5. The adoption of the form of discharge vessel shown in fig. 1 does not wholly remove the uncertainty concerning the speed with which the positive ions strike the metal which they disintegrate; for the ions are produced throughout the volume of the vessel and the speed with which they reach the grid will depend upon the potential relative to the grid of the place where they are formed. But if the pressure of the gas is so low that the mean free path of the ions is greater than the dimensions of the vessel, the relation of this speed to the nature of the gas and the conditions of the discharge will be comparatively simple, and probably much simpler than it is when the discharge is unsupported and the ions are travelling to the cathode through an abnormal cathode fall. For if the thermionic current is saturated (as it always was in these experiments) and the "space charge" neutralized, the distribution of potential throughout the vessel will be determined almost wholly by the geometrical form of the electrodes and of the walls. Further if collisions of the ions with molecules are rare, the speed of an ion reaching the grid will be simply that corresponding to the difference of potential between the grid and the place where the ion was formed. The distribution of these places will be almost independent of the nature and pressure of the gas, since, apart from small differences due to differences in the ionization potential, it will depend on the chance of an electron colliding with a molecule. Accordingly the mean energy of the ions reaching the grid should be independent of the nature and pressure of the gas and of the thermionic current.

In these circumstances, if the disintegration of the grid is determined by the number and energy of the positive ions reaching it, S should be independent of the pressure of the gas and the thermionic current; it should be a function of

6. It was important to determine at the outset whether a pressure low enough to satisfy these conditions could be attained and yet the rate of disintegration remain large enough to be measurable. Examination of the characteristic of the discharge, and especially of the ratio of the grid to the anode current, suggested that the necessary conditions could be obtained; but the most conclusive evidence is obtained by measuring the disintegration with the same V_0 at different pressures and different thermionic currents.

Neon-Helium
 $V_0 = 330$ volts

Pressure (mm)	S
0.005	0.130
0.010	0.132
0.012	0.135
0.015	0.125
0.018	0.138
0.020	0.128
0.025	0.128
0.028	0.115
0.032	0.130
0.035	0.145
0.040	0.125
0.042	0.115
0.045	0.118
0.050	0.110
0.055	0.112
0.060	0.098
0.065	0.098
0.070	0.075
0.072	0.070
0.075	0.075
0.080	0.065
0.085	0.062
0.088	0.035

Fig. 2 shows the result of one series of measurements at different pressures, the gas being a mixture of atmospheric neon and helium containing about 25 per cent. of the latter.

It will be seen that at pressures below $\cdot 025$ mm., S is independent of the pressure, while at higher pressures S decreases as the pressure increases. That result is completely in accordance with expectation, for at the higher pressures the ions will collide with molecules on their way to the grid, and the mean energy with which they arrive will be correspondingly reduced. Similar results were obtained in other gases; the pressure below which S becomes constant varies; it is greater for gases with long free paths (H_2 , He) than for those with short free paths (Hg). All the measurements recorded below were made at pressures on the flat part of the curve. Again, many experiments were made to determine whether S was independent of the thermionic current. It was suspected that there might be some dependence because the ratio i_g/i_a decreased somewhat as i_a increased. This variation of i_g/i_a is doubtless due to recombination. In a vessel such as that used, with electrodes of area small compared with that of the walls, it is known * that some of the electrons follow very long paths, in the regions of weak field, so that the opportunities for recombination are considerable. This recombination might remove chiefly the ions which, if they arrived at the grid, would have little energy and cause little disintegration, so that an increase of S with i_a might have been anticipated. But no evidence of a dependence of S on i_g or i_a could be detected; the proportion of the ions of given speed disappearing by recombination must be approximately independent of that speed.

Lastly, it appeared that S was independent within wide limits of the potential of the cathode. Indeed V_a was of very little importance from any point of view so long as V_0 was constant; it could often be varied from $0\cdot95 V_0$ to $0\cdot5 V_0$ without a variation of more than a few per cent. in i_a or i_g . This independence of the discharge of the cathode potential is to be expected. For as long as the field at the cathode is sufficient to saturate, the thermionic emission i_a (which is always large compared with i_g) will be independent of V_a . Again, since the field is intense round the cathode, and V_a is large compared with the ionization potential, the volume within which the electrons have not yet gained the ionizing energy will be a small fraction of the whole volume of the vessel; consequently the number of ions formed per electron will not vary rapidly with V_a .

* Research Staff of G.E.C. Ltd., Phil. Mag. xlii. p. 230 (1921).

Results.

7. When these preliminary matters were settled and the method of investigation proved reliable, the factors determining disintegration could be investigated.

First it was shown that the impact of positive ions is necessary for disintegration. If V_g was negative, so that the grid acted as an anode, there was no disintegration whatever. Again when, as in the normal arrangement, V_g was positive, and the grid deflected from the cathode all but a very small proportion of the ions, very little disintegration of the cathode occurred. Definite measurements of the disintegration of the cathode were not made, but, by working with the grid sufficiently negative, it was possible to remove one-half of the material of the grid before the resistance of the cathode had increased by 1 per cent.

Second, it was shown that S is independent within wide limits of the temperature of the grid. Comparative experiments, made first with the grid relatively cold (it was always heated by the discharge to about $200^\circ\text{C}.$), and then with the grid heated by a battery to about $1200^\circ\text{C}.$, disclosed not the smallest variation of the disintegration with the temperature. Higher temperatures were not used, because when thermionic emission from the grid begins, i_g is no longer a measure of the positive ions striking it. S was smaller than the normal for a newly inserted grid, but became normal as soon as surface impurities were removed.

Third, the rate of disintegration was determined for values of V_0 up to 700 volts in the following gases:—Hydrogen, helium, nitrogen, atmospheric neon-helium mixture, mercury vapour, argon. The results are shown in figs. 3 and 4. It was not possible to examine all these gases fully in a single vessel; for before sufficient observations have been made the disintegration of the grid has proceeded too far. But the observations in two vessels, which are shown in the figures, include between them all the gases mentioned. It is not to be expected that the absolute values of S in the two vessels will agree, because (see § 5) the same value of V_0 will correspond to different values of the mean energy, owing to slight differences in the distances between the electrodes. But the relations between the lines for the four gases which appear in both figures (Ar, Hg, Ne-He, He) are in general the same in each. Accordingly, the following conclusions seem justified:—

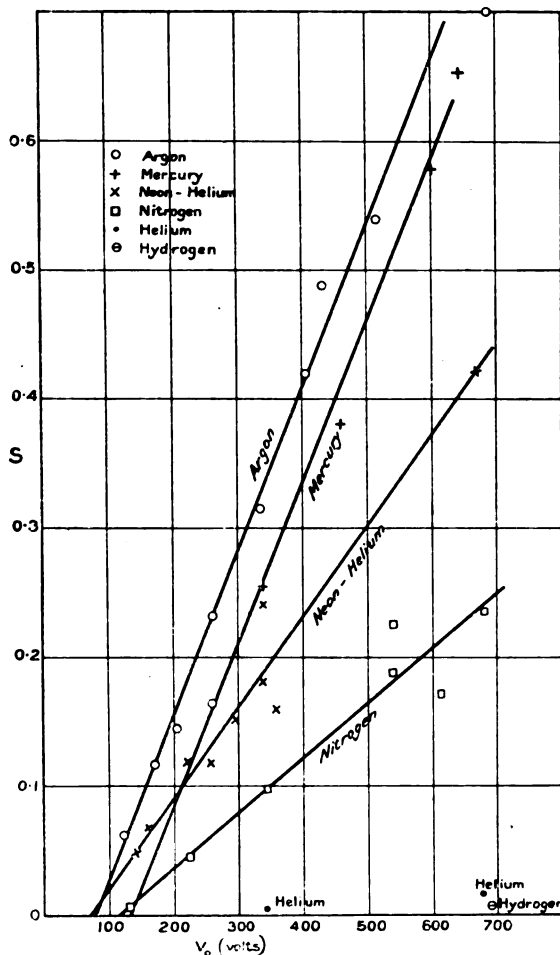
(a) The relation between S and V_0 is approximately of

the form

$$S = a(V_0 - V_0'), \dots \dots \dots (10)$$

where V_0' is not much greater than 100 volts. There was some tendency for the lines in figs. 3 and 4 to be concave to the horizontal axis, but as the observations were not

Fig. 3.



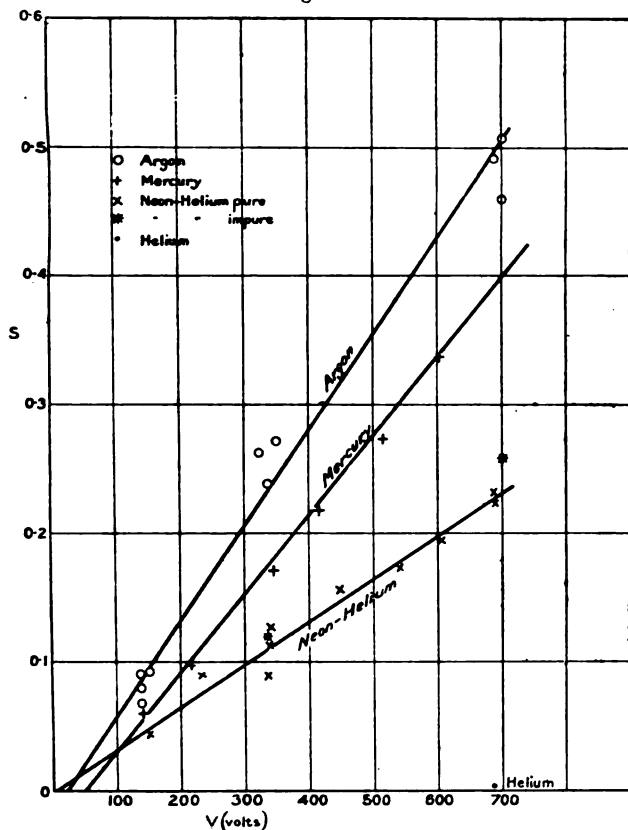
sufficiently accurate to determine the curvature the lines are drawn straight.

S may be greater than $\frac{1}{2}$. Since Cheney (*loc. cit.*), who presumably measured the current carried by charged atoms as well as by electrons, found the ratio of the negative

particles leaving to positive particles incident to be less than 0.1, it seems to follow that the metal particles are initially uncharged. In accordance with this view is the fact that there was no concentration of blackening round the anode.

(b) If the gases are placed in order of increasing magnitude for a given V_0 , the series runs H_2 , He, N_2 , Ne-He, Hg, Ar, the difference between S for the two extreme numbers of this series being of the order of 100 to 1.

Fig. 4.



Attempts were made to measure S for potassium vapour. The discharge vessel was thoroughly evacuated and sealed off from the pump with a small quantity of the metal condensed on the walls; it was maintained in a small oven at about 100°C . in order that the vapour pressure of the metal might be sufficient to give a value of i_p of the same order as that given by the other gases. The experiments are difficult

and have not yet been carried to a successful conclusion. As far as they have gone they indicate that S for potassium vapour is of the same order as that for nitrogen—much more than for He, and much less than for Ar. This vapour was investigated because of the remarkable fact, discovered by the General Electric Company of America *, that a discharge giving a strong luminous glow with thermionic emission from a tungsten cathode can be maintained in sodium vapour (and apparently other alkali metal vapours) for many hours without serious disintegration of the tungsten.

Since they were using a pressure of the vapour of $\cdot 05$ mm., the disintegration due to the discharge would be somewhat smaller than that calculated from S and the potential between the electrodes, because the mean free path would not be large compared with the distance between the electrodes, and the ratio of the mean to the maximum possible energy of the ions would be low. But our observations (if they are confirmed) agree with theirs in so far that S for metals (Hg, K) appears to be very much less than that for inactive elements of the same molecular weight.

8. In view of the remarkable decrease of disintegration in the independent discharge through the inactive gases produced by the addition of small traces of impurity (see p. 99), some experiments were undertaken on mixtures of argon, and of neon-helium with hydrogen and nitrogen. Quantitative measurements were difficult because the hydrogen and nitrogen disappear in the discharge much more rapidly than the inactive gases, so that after the discharge has lasted a short time the composition of the gas has changed. But the observations were sufficient to show that the effect found by Pintsch is not reproduced in the conditions of these experiments. (We do not mean to imply the smallest doubt that it is obtained in the conditions which he describes; indeed, we have been able to repeat all his observations.) Thus when 25 per cent. of H_2 was mixed with Ar, no certain decrease of S was produced; the absence of any decrease was doubtless due to the fact that Ar molecules were ionized, owing to their greater diameter, rather than the hydrogen. Similarly a mixture of 1 part (Ne-He) and 2 parts H_2 gave a value of S about half that of the (Ne-He) mixture. This mixture was known to contain at least 1 per cent. of impurity, probably N_2 , and yet removal of this impurity by means of charcoal and liquid air produced no increase in S , but rather a decrease—which was doubtless due to the fact that the cooled charcoal removed more of the Ne than of the He. The points for the impure gas are shown on fig. 1.

* Brit. Patent 175032.

It was found that when a mixed gas was used, the ratio of S for the mixture to that for the pure constituents varied considerably with V_0 . The explanation is doubtless that the proportion of the two constituents which are ionized varies with V_0 . This observation explains why the line for the Ne-He mixture in figs. 2 and 3 cuts the lines for the pure gases.

9. The discharge which causes the disintegration is always accompanied by a decrease in the pressure of the gas; the gas disappears slowly, being absorbed in, or on the surface of, the metal deposited on the walls. This disappearance of the gas has been described by us in some detail in earlier papers. The experiments of this paper were not well adapted for studying the process, since the volume of gas in connexion with the discharge vessel was large and the measurement of pressure not very accurate. But some conclusions which are just worth record were reached.

The only gases which can be compared in this matter are argon, neon, helium, and nitrogen; for the disappearance of hydrogen is known to be anomalous, and that of the vapours could not be measured easily. Further, since the neon used was mixed with helium, conclusions concerning it are doubtful. It was found that the amount of gas disappearing per coulomb of positive ions reaching the grid was of the same order of magnitude whether the gas was neon-helium, helium, or nitrogen; a factor of 4 or less will cover all three gases. Nitrogen probably disappears most rapidly and helium least rapidly. The disappearance of argon is notably less than that of these three gases; indeed, it could never be established certainly that it disappeared at all. It follows that the gas disappearing per unit mass of metal deposited on the walls is far greater for helium than for the other gases, since the mass per coulomb is far less. It appears therefore that the rate of disappearance is determined by the rate of ionization of the gas rather than by the rate of deposition of metal; the disappearance cannot be explained simply as a trapping of the gas by the deposited metal. Probably the rate of deposition is important only in so far as it provides fresh surfaces to which the gas may adhere in the manner suggested by us in a previous paper*.

Conclusions.

10. The conclusion we would draw from these experiments is that the rate of disintegration S is a definite function of the nature of the positive ions and of their energy, increasing with the latter. There is no evidence that S is zero for any

* Research Staff of the G. E. C. Ltd., Phil. Mag. xliii. p. 914 (1922).

value of V_0 less than the ionization potential—for the prolongation of the lines to cut the axis cannot be relied on—and there is no evidence of any exceptional change in S when V_0 is in the neighbourhood of the normal cathode fall, which varies from about 140 volts for Ne to 330 for H_2 . Further, there is no immediately obvious connexion between S for a given V_0 and the other properties of the ion. In general S increases with the mass of the ion, as other workers have found, but the order of Ar and Hg, and (probably) of Ne and K are exceptions. Again, the inactive gases appear especially active in disintegration, but here He is an exception. On the other hand, it appears that the metals may be especially inactive. These relations are very puzzling, and as yet we offer no theory to explain them; the next step in developing an adequate theory of cathode disintegration must be to correlate the disintegrating power of an ion with some other of its properties.

But it is already possible to see that information derived from such experiments as these will throw light upon the problems of the unsupported discharge. Thus, in that form of discharge, the loss of mass by disintegration per coulomb carried between the cathode and the anode is proportional to $V - V'$, where V is the potential between the electrodes, and V' of the order of the normal cathode fall; *e.g.* Kohl-schütter gives $V' = 495$ volts for air. There is practically no sputtering so long as the cathode fall is normal. Interpreted in the light of our experiments, this must mean that with a normal cathode fall, either the current at the cathode is conveyed almost wholly by electrons, or, more probably, that the positive ions arrive at the cathode with energies far less than that corresponding to the normal cathode fall. It is only when the cathode fall is abnormal that the positive ions strike it with any considerable velocity.

Again, the reduction of the disintegration with abnormal cathode fall in the inactive gases due to the presence of small quantities of impurity must mean either that the energy of the ions arriving at the cathode is reduced or that ions of the impurity, rather than of the inactive gas, carry the current to the cathode. Since mercury is as effective as other impurities, the first alternative seems the more probable.

Generally, measurements of disintegration will enable a distinction to be made between current conveyed by positive ions arriving at an electrode and by electrons leaving it. In the hope of applying the knowledge gained to such problems, we propose to carry these problems further, and, in particular, to get a more definite relation between S and the energy of the ions.

VIII. *On the Molecular Scattering of Light in Dense Vapours and Gases.* By C. V. RAMAN, M.A., Hon.D.Sc., Palit Professor of Physics in the Calcutta University; and K. R. RAMANATHAN, M.A., Demonstrator in Physics, Maharajah's College, Trivandrum, and University of Madras Research Scholar*.

1. Introduction.

AS is well-known, the theory advanced by the late Lord Rayleigh† explaining the blue light of the sky as due to the molecular scattering of sunlight has of recent years been amply confirmed by accurate measurements of sky-radiation and of the attenuation of the sun's rays in traversing the earth's atmosphere, and also by the laboratory experiments of Cabannes‡ and of the present Lord Rayleigh§ which have demonstrated the scattering of light by dust-free gases and shown that its magnitude is in agreement with the theory. Apart from its special application to the explanation of the blue light of the sky, the subject of the molecular scattering of light possesses very great interest, standing as it does in intimate relationship with the fundamental problems of optics, such as the propagation of light and the reflexion, refraction, dispersion, and extinction of light in transparent media. Its study has already yielded information which is of first-rate importance in testing theories of atomic and molecular structure, and promises to prove even more fruitful in future in the same direction. It is also not improbable that the study of the problems of molecular scattering of light may serve to elucidate the nature of radiation itself, that is, to determine whether it consists of some form of continuous disturbance moving through space, as contemplated by Maxwell's electromagnetic theory, or whether it consists of discrete entities or "quanta," as conceived of by Einstein. It is proposed in this paper to consider the very important problem of the scattering of light in *dense* media, such as vapours and gases under high pressure, in which circumstances, as was pointed out by the late Lord Rayleigh himself, the simple treatment proposed by him is not applicable. Fresh experimental evidence bearing on the subject will also be referred to.

* Communicated by the Authors.

† Phil. Mag. xlvii. pp. 375-384 (1899). Scientific Papers, vol. iv. p. 397.

‡ *Annales de Physique*, xv. pp. 1-150.

§ Proc. Roy. Soc. xciv. p. 453 (1918) *et seq.*

Phil. Mag. S. 6. Vol. 45. No. 265. Jan. 1923..

2. *Rayleigh's Theory of Light-Scattering.*

As a preliminary to the discussion of the problem of light-scattering in highly compressed gases and vapours, it is useful to recall very briefly the principles on which the case of gases under ordinary conditions was dealt with by Lord Rayleigh. Reduced to its essentials, the treatment is on the following lines:—

The individual molecules in a gas through which the primary waves of light pass are regarded as secondary sources of radiation, each molecule acting more or less as it would in the absence of its neighbours. There is, of course, a definite phase-relation between the primary wave when it reaches a given molecule and the secondary wave emitted from it. *In the direction of propagation of the primary waves* the secondary radiations emitted by all the molecules in a given layer are in identical phase, for the differences in the phase of the primary wave when it reaches different molecules are exactly compensated by the acceleration or retardation due to the scattered waves having to traverse a shorter or greater path, as the case may be. *In other directions*, however, owing to the molecules being distributed at random within the volume of the gas, the phases of the scattered waves do not stand in any invariable relation to each other, and hence, in order to find the average expectation of intensity of the scattered light emerging from within the gas, the *intensities*, not the amplitudes of the waves scattered by the individual molecules, should be added up. In all ordinary cases there is very little difference of phase between the primary wave reaching an individual molecule and the secondary wave sent out by it so far as the direction of original propagation of the wave is concerned. When, however, the effect of all the molecules contained in a stratum parallel to the plane of the primary wave is integrated by the usual method of subdivision of the stratum into Fresnel zones, and the resultant is combined with the primary wave, a change of phase appears which may be identified as the retardation associated with the passage of waves through a refractive medium. A relation is thus obtained between the scattering power of the molecules, their number per unit volume, and the refractivity of the medium. Thus, taking the light-vector in the primary waves to be represented by $R_0 \cos(\omega t - lx)$, where x is measured from the position of the scattering molecule, the vector in the scattered wave arising from it may be written as

$$A_1 \cos(\omega t - lr) R_0 \sin \theta / r, \quad . \quad . \quad . \quad (1)$$

when r is the distance from the molecule and θ is the angle between the vibration at the origin and the scattered ray. On carrying out the calculations indicated, the relation obtained is

$$n_1 A_1^2 = \frac{4\pi^2(\mu-1)^2}{n_1 \lambda^4}, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where n_1 is the number of molecules in unit volume, λ is the wave-length of the light, and μ is the refractive index of the gas.

The energy scattered by the molecules in the interior of the gas must be derived from the primary beam, and hence the intensity of the latter must suffer an attenuation as it passes through the medium. The coefficient of attenuation may be readily evaluated by a simple calculation of the total energy scattered by an individual molecule, and then multiplying this by the number n_1 of molecules per unit volume. We thus obtain the intensity of the transmitted light to be $I = I_0 e^{-kx}$, where k the coefficient of attenuation is given by the relation

$$k = \frac{32\pi^3(\mu-1)^2}{3n_1 \lambda^4}. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

This expression for the attenuation coefficient may also be derived directly by a more accurate investigation, which does not neglect the small difference of phase between the primary wave and the secondary waves originating at a molecule. It is then found that on compounding the effects of the primary wave with those of the secondary wave arising from a stratum of molecules, there appears, in addition to the alteration of phase of the primary wave, also a small diminution in its intensity which is exactly that expected in view of the lateral scattering of part of the energy.

3. Justification of the Principle of Random Phase.

It will be seen from the foregoing that the Rayleigh law of scattering depends for its validity on the principle that the phases of the waves laterally scattered by the individual molecules are absolutely at random. This point is clearly brought out in the detailed analyses of the problem which have been given H. A. Lorentz * and by the late Lord Rayleigh himself †, and it appears that the necessary random character of the phases of the scattered waves can only arise

* • Proc. Roy. Soc. of Sciences, Amsterdam, xiii. p. 92 (1910).

† Phil. Mag. xxxvi. pp. 429-449 (1918).

from a random arrangement in space of the molecules under consideration. If we deny the random character of this distribution of phase of the scattered waves, we must also deny the applicability of Rayleigh's law expressing the intensity of the scattered light in terms of the refractivity of the medium. The fact that even in a gas at atmospheric pressure there are about 10^6 molecules in a cube of the size of a wave-length of light, so that the scattered waves arising from adjacent molecules differ in phase by only 10^{-2} of the period, has been felt as a difficulty by some writers in this connexion. In fact, Larmor* has raised the question whether in view of this closeness of packing we are really justified in considering the phases of the individual scattered waves to be distributed entirely at random. It may be easily shown, however, that no appreciable deviation from a random distribution of phase, and therefore, also, from the Rayleigh law of scattering, can arise so long as the pressure-volume relation of the gas does not sensibly deviate from Boyle's law. For, all that is necessary is that the chance that a given molecule finds itself in a specified finite element of volume should be a random one, that is, is sensibly uninfluenced by the other molecules in the gas. This is true provided the total volume occupied by all the molecules, or rather by all their spheres of mutual action, forms a small fraction of the total space in the containing vessel, which is obviously also the condition that the compressibility of the gas should not appreciably deviate from that given by Boyle's law.

Larmor has made the suggestion † that Rayleigh's principle of random phase is not correct in the form in which it is stated, but that the random character of the phases of the scattered waves when they reach the observer is secured by the Doppler effect, due to the motion of the scattering molecules. The view he proposes is, in fact, that the phases of the scattered radiations emerging from the column of gas may be correlated at first, but after traversing 10^6 wave-lengths, or 50 cms., they would have become fortuitous and the energy-effects thus additive. Larmor's suggestion is, however, not acceptable. For, if it were correct, we should find that the aggregate intensity of the scattered light should be small immediately after emergence from the column of gas, that is, when it is observed within a distance of a centimetre or two from the track of the primary beam, and should increase at a greater distance from it. Such a result is

* Phil. Mag. xxxvii. p. 161 (1919).

† Loc. cit.

obviously quite inadmissible, besides being contrary to experience. The fallacy lies in Larmor's assumption that the change of wave-length (Doppler effect) has an effect on the relative phases of the scattered waves, whereas in reality it has none. To make this clear, we may consider two neighbouring molecules A and B. The scattered waves originating from them travel outwards with an identical velocity which is quite unaffected by any movements of these molecules. The phase-difference at any epoch therefore remains unaffected as the waves move out, being exactly the same as when the portions of the wave-train under consideration left the molecules. In other words, the phase-difference at each stage is exactly the same as if the molecules had remained fixed from the instant of emission of the scattered light. The scattering from any appreciable volume of gas would thus remain unaffected if all the molecules were assumed suddenly to be fixed in their instantaneous positions, and the Doppler effect due to their movement exerts no influence whatever on the observed results. Larmor's suggestion, therefore, clearly fails, and we have to fall back upon the view already expressed that the *principle of random phase of the scattered waves rests upon the random character of the distribution of the molecules in space in a gas obeying Boyle's law.*

4. Application of Boltzmann's Distribution Law.

It is clear from the preceding discussion that if the distribution of the molecules of a gas or vapour in space is *not* a random arrangement, the intensity of the light scattered would not be given by the Rayleigh law, that is, would cease to be simply proportional to the number of molecules per unit volume. In the usual treatments of the kinetic theory of gases, the molecules are conceived to exert forces on each other, and if the time during which the forces acting on any individual molecule are sensible forms an appreciable fraction of the whole time, the arrangement of the molecules would not be a random one. The influence of the molecules on each other would not then be negligible, and the energy-effects of the individual molecules could not be added up to find the total light scattered in the manner contemplated by the simple theory. It is, however, possible to make a calculation of the altered scattering power of the gas. Let $\phi(r)$ be the law of repulsive force between any two molecules whose centres are at a distance r from each other. By a suitable assumption regarding the nature of $\phi(r)$, it is possible to

include in this function the cohesive or van der Waals's forces which act when the molecules are not in collision with each other, and also the large repulsive forces occurring during actual impact. According to a well-known theorem due to Boltzmann*, the chance that two molecules find themselves at a finite distance r apart is less than the chance that they are at a very great distance apart in the ratio

$$e^{-\frac{1}{RT} \int_r^\infty \phi(r) dr}, \quad \dots \dots \dots (4)$$

where $\int_r^\infty \phi(r) dr$ obviously expresses the potential energy of the configuration. The probability of groups of three, four, or more molecules being found at specified distances apart may be similarly expressed in terms of the potential energies of the respective configurations. If we assume that the deviation from Boyle's law is not very large, expression (4) will suffice to enable us to take into account the mutual influence of the molecules in determining their ordering in space. Consider a sphere of radius l drawn round the instantaneous position of a given molecule as centre. If n be the whole (actual) number of molecules in the volume of the gas or vapour, the number to be expected within this sphere of volume $\frac{4}{3}\pi l^3$ is

$$\int_0^l A \cdot 4\pi r^2 dr e^{-\frac{1}{RT} \int_r^\infty \phi(r) dr} \quad \dots \quad (5)$$

where A is a constant to be presently determined. Integrating by parts, (5) reduces to

$$A \left[\frac{4}{3} \pi r^3 e^{-\frac{1}{RT} \int_r^\infty \phi(r) dr} - \frac{1}{RT} \int_0^l \frac{4}{3} \pi r^3 \phi(r) dr e^{-\frac{1}{RT} \int_r^\infty \phi(r) dr} \right]_0^l \quad (6)$$

To enable this expression to be reduced, we will assume that the force $\phi(r)$ between two molecules vanishes sensibly when $r \geq \sigma$, where σ is the range of molecular action. The expression (6) then reduces to

$$A \cdot \frac{4}{3} \pi l^3 - \frac{A}{3RT} \int_0^\sigma 4\pi r^2 r \phi(r) dr e^{-\frac{1}{RT} \int_r^\infty \phi(r) dr}, \quad \dots \quad (7)$$

provided $l \geq \sigma$. When l is very great, the first term in (7) will be very large in comparison with the second, and since (7) must then give the total number of molecules, we find at once $A = \frac{n}{v}$. We may denote the integral in (7) by C ;

* *Vorlesungen über Gastheorie*, II. See also Jeans' 'Dynamical Theory of Gases,' 3rd ed. p. 132.

and putting $l=\sigma$, we find that, on the average, the number of molecules which we may expect to find within the sphere of action of the specified molecule is

$$\frac{n}{v} \cdot \frac{4}{3} \pi \sigma^3 - \frac{nC}{v \cdot 3RT}, \quad \dots \quad (8)$$

and is thus smaller than the number corresponding to a random distribution of the molecules by $\frac{nC}{v \cdot 3RT}$. (If C be negative, the number will be greater.)

In order to evaluate the intensity of the scattered light, we may now apply the general method developed by the late Lord Rayleigh*. The disturbance due to the scattered waves may be represented by the summation

$$\sum \cos(pt + \epsilon_1), \quad \dots \quad (9)$$

where ϵ_1 represents the phase of the scattered wave arising from a molecule and is easily expressed in terms of the position of the molecule and the directions of the incident and scattered rays. The intensity of the scattered light is obviously represented by

$$\begin{aligned} & [\cos \epsilon_1 + \cos \epsilon_2 + \cos \epsilon_3 + \dots]^2 \\ & + [\sin \epsilon_1 + \sin \epsilon_2 + \sin \epsilon_3 + \dots]^2 \\ & = n + 2 \sum \cos(\epsilon_1 - \epsilon_2), \quad \dots \quad (10) \end{aligned}$$

where n is the number of molecules and the summation $\sum \cos(\epsilon_1 - \epsilon_2)$ has to be made for all the $\frac{1}{2}n(n-1)$ pairs of molecules contained in the volume. For a random distribution, $\sum \cos(\epsilon_1 - \epsilon_2)$ vanishes, as has been shown by Lorentz and by Rayleigh. In the present case, the distribution differs from a random one in that the average number of molecules present within the sphere of action of a molecule is smaller by $\frac{n}{v} \frac{C}{3RT}$. The summation indicated in (10) will

not therefore reduce to n simply. Since the radius of action σ of the molecules is much less than the wave-length of the light, the value of $(\epsilon_1 - \epsilon_2)$ for the missing molecules may without appreciable error be taken to be zero, and hence, when the summation is carried out for all the molecules in the volume v , (10) will reduce to

$$n \left(1 - \frac{n}{v} \cdot \frac{C}{3RT} \right). \quad \dots \quad (11)$$

* Phil. Mag. xxxvi. pp. 429-449 (1918).

From this it is seen that if C be positive, the intensity of the scattered light is less than that given by the Rayleigh law, while if C be negative, it is *greater*.

In order to interpret the result contained in (11), we notice that the integral in the second term of (7) which we have denoted by C when multiplied by $\frac{1}{2} \frac{n^2}{v^2}$ represents the *virial function* for the gas or vapour. The virial equation is in fact simply *

$$pv = nRT + \frac{1}{6} \frac{n^2}{v} C. \quad . \quad . \quad . \quad . \quad . \quad (12)$$

By differentiating (12), the compressibility β of the gas or vapour may be written as

$$\beta = -\frac{1}{v} \frac{dv}{dp} = -\frac{1}{n} \frac{RT}{v} \left(1 + \frac{n}{v} \frac{C}{3RT} \right) \quad . \quad . \quad . \quad (13)$$

$$= -\frac{v}{nRT} \left(1 - \frac{n}{v} \frac{C}{3RT} \right), \quad . \quad . \quad . \quad . \quad . \quad (14)$$

to the same degree of approximation as used previously. On comparing (14) with (11), it is seen that the intensity of the light scattered per unit of volume, instead of being proportional to $\frac{n}{v}$ as required by the Rayleigh law, is proportional to

$$\frac{n^2}{v^2} RT\beta, \quad . \quad . \quad . \quad . \quad . \quad (15)$$

and thus varies directly as the absolute temperature, the square of the density of the substance and its compressibility.

In the case of a gas obeying Boyle's law, $\beta = \frac{1}{p}$ and $pv = nRT$, and (15) becomes simply $\frac{n}{v}$ in agreement with the Rayleigh law.

5. *The Theory of Density Fluctuations.*

The result deduced by us in the preceding section from the principles of the kinetic theory for the case of moderately compressed gases agrees with the general formula obtained

* This agrees with Keesom's approximate equation of state, containing only the first two terms in the expansion of the virial function. Proc. Roy. Acad. Sciences, Amsterdam, vol. xv. p. 264.

in an entirely different manner by Einstein * in developing an explanation given by Smoluchowski † of the phenomenon of opalescence exhibited by fluids in the vicinity of the critical state. Einstein's reasoning is of a very general character and makes no use whatever of the molecular hypothesis. It is based on the following train of ideas. If, in the condition of equilibrium, the medium is conceived of as a completely uniform homogeneous system, there can be no scattering of the light-waves passing through it. Actually, however, as Smoluchowski showed from thermodynamical considerations, the density of the substance must vary from point to point, and also fluctuate from instant to instant, the density as measured by our ordinary appliances being merely a statistical average. Hence, in framing the electromagnetic equations, the dielectric constant (which is assumed to vary with the density in the manner contemplated by the Lorentz-Mossotti formula) must be regarded as varying from point to point, and the solution of the equations for wave-propagation contains, besides the regularly transmitted waves, also an opalescence radiation which is a volume-effect and represents the scattered light resulting from the local inequalities of density. Einstein's treatment naturally therefore falls into two parts: firstly, the determination of the magnitude of the fluctuations of the dielectric constant for the elements of volume, secondly, the calculation of the opalescent radiation.

The magnitude of the density-fluctuations is calculated by Einstein in the following manner:—Boltzmann's well-known thermodynamical principle connects the entropy S of a system with the probability W to which the entropy S relates by the equation

$$S = R \log W + \text{constant}, \quad (16)$$

where R is the gas-constant. Einstein points out that the entropy S of the whole system does not completely define the physical conditions of the small individual parts of the system at any instant, and hence (16) should be understood as referring to an *ensemble* of different possible conditions of the system in each of which its entropy is S . If we consider particular parts of the system and particular instants of time, fluctuations from the ideal thermodynamic equilibrium must appear, the magnitude of which is determined by the corresponding changes of entropy of the parts of the system. For an isothermal compression or rarefaction, the change of

* *Annalen der Physik*, xxxiii. p. 1294 (1910).

† *Loc. cit.* xxv. p. 205 (1908).

entropy is simply the work done divided by the absolute temperature. Boltzmann's theorem may be written in the form

$$W = e^{\frac{S - S_0}{R}}, \quad \dots \quad (17)$$

where S_0 is the entropy in the state of thermodynamic equilibrium. Taking ν to be the deviation of some observable physical variable, *e. g.* in this case the density, from the value corresponding to thermodynamic equilibrium, Einstein writes (17) in the form

$$W(\nu)d\nu = Ae^{-\frac{1}{2RT}a\nu^2}d\nu, \quad \dots \quad (18)$$

where $W(\nu)d\nu$ is the probability that ν lies between ν and $\nu + d\nu$, A is a constant, and $\frac{1}{2}a\nu^2$ is the work done in altering ν from 0 to ν . (18) evidently has the same form as Gauss's error-law, and it follows that

$$\overline{\frac{1}{2}a\nu^2} = \frac{1}{2}RT, \quad \dots \quad (19)$$

where the bar indicates the *mean* value of the quantity under consideration. If we identify ν with $(\Delta\rho)$ the fluctuation of density, its mean square may be evaluated from (19) and written in the form

$$(\overline{\Delta\rho})^2 = -\frac{RT\beta\rho_0^2}{\phi}, \quad \dots \quad (20)$$

where β is the isothermal compressibility, ϕ is the small element of volume under consideration, and ρ_0 is the mean density.

For the deduction of the light-scattering from (21) with the aid of Maxwell's electromagnetic equations, reference should be made to Einstein's original paper. We may follow here an abbreviated treatment which gives an identical result.

At right angles to the incident light the intensity of scattered light is given by the expression *

$$\frac{\pi^2\phi^2(\Delta\epsilon)^2}{2\lambda^4} \frac{1}{r^2}, \quad \dots \quad (21)$$

$(\Delta\epsilon)$ being the variation of the dielectric constant.

Now, as the individual local variations of the dielectric constant are irregularly distributed, the phases of the various scattered beams are also quite arbitrary, and hence for calculating the total intensity of scattered light we have

* Rayleigh, Phil. Mag. p. 81 (1881); Sc. Papers, vol. i. p. 526.

merely to sum up the above expression over the total volume v . The expression contains a factor

$$\Sigma(\Delta\epsilon)^2\phi^2,$$

which may be evaluated by use of the Mosotti-Lorentz law

$$\frac{\epsilon-1}{\epsilon+2} = \text{const. } \rho.$$

Differentiating, we obtain

$$(\Delta\epsilon)^2 = \frac{(\epsilon-1)^2(\epsilon+2)^2}{9} \left(\frac{\Delta\rho}{\rho_0} \right)^2. \quad (22)$$

Substituting in this the value given above for fluctuation of density, we obtain

$$\frac{(\epsilon-1)^2(\epsilon+2)^2}{9} RT\beta \Sigma \phi = RT\beta \frac{(\epsilon-1)^2(\epsilon+2)^2}{9} \cdot v. \quad (23)$$

Thus the intensity of light scattered by a cubic centimetre of fluid at right angles to the incident rays is

$$\frac{\pi^2}{18} RT\beta \frac{(\epsilon-1)^2(\epsilon+2)^2}{\lambda^4} = \frac{\pi^2}{18} RT\beta \frac{(\mu^2-1)^2(\mu^2+2)^2}{\lambda^4}. \quad (24)$$

In the cases of gases and vapours, whether obeying Boyle's law or not, the formula (24) may be appreciably simplified by assuming $(\mu^2+2)=3$, and $(\mu^2-1)^2=4(\mu-1)^2$ approximately, and it may then be written in the form

$$\frac{2\pi^2(\mu-1)^2 RT\beta}{\lambda^4}. \quad (25)$$

If the gas or vapour obeys Boyle's law, $\beta = \frac{1}{p}$ and $pv = nRT$, and (25) becomes identical with the Rayleigh law. In other cases, (25) is seen to agree with formula (15) when the omitted multiplying factors are restored.

It may be pointed out that the expression giving the magnitude of the density-fluctuation might have been derived immediately from the principle of equipartition of energy, as is indeed evident from the form of the relation (19). In the case of a gas obeying Boyle's law in which the molecules are distributed at random throughout the space, the mean square of the density-fluctuation may also be derived by direct application of the theory of probabilities, and the intensity of the scattering calculated therefrom. This has been done by Lorentz*, and the result naturally agrees with that obtained by Rayleigh.

* Proc. Roy. Soc. Amsterdam, xiii. p. 92 (1911).

6. *Experimental Tests of the Einstein-Smoluchowski Formula.*

The expression given by Einstein for the light-scattering in a direction transverse to the primary beam, viz. :

$$\frac{\pi^2}{18} \frac{R_1 T \beta}{N_1} \frac{(\mu^2 - 1)^2 (\mu^2 + 2)^2}{\lambda^4},$$

where R_1 and N_1 represent the gas-constant and the Avogadro-number respectively for a *gram-molecule*, was originally developed by him to explain the opalescence exhibited by fluids in the vicinity of the critical state. It should, however, possess a far wider and *general* application, and indeed be regarded as superseding the Rayleigh law of scattering, which should only be valid in the special case of gases accurately obeying Boyle's law. It is thus of great importance to test the validity of the Einstein-Smoluchowski formula over a very wide range of cases. So far as the authors are aware, the only experimental tests that have so far been made of it for the case of a single substance in the gaseous state are those of Kammerlingh Onnes and Keesom* on the opalescence of ethylene vapour, but the work of these investigators was confined to a range of only 2.5 degrees of temperature *above* the critical temperature of this substance. A far more comprehensive and general test of the formula for several substances over the widest possible range of temperatures and pressures is obviously desirable, and researches with this object have been undertaken in the authors' laboratory. The first substance chosen was ether. This substance has a high refractivity and therefore a large scattering power in the state of vapour, and its critical temperature and pressure are moderate, and it also possesses a high degree of chemical stability under the action of heat and light. It is therefore very well suited for quantitative work. The detailed account of the determinations carried out with it by one of us (K. R. Ramanathan) will be published in a separate paper, and it will suffice here to indicate the general scope of the work and the results obtained. The light-scattering power of ether has been determined separately for the substance in the saturated vapour and in the liquid phases for temperatures from 30° C. to the critical temperature 194° C., and for the gaseous phase from 194° C. to 217° C. The vapour and gaseous phases deviate very largely from Boyle's law, the compressibility being larger than the reciprocal of the pressure, especially at the higher temperatures, and the

* *Loc. cit.* (1908).

measurements throughout the whole range show that the *Rayleigh law of scattering completely breaks down* and strikingly confirm the correctness of the Einstein-Smoluchowski formula. The scattering power of the vapour when it is dense is in fact several times larger than that given by the Rayleigh law, and this feature is more and more pronounced as the critical temperature is approached from either side. The Einstein-Smoluchowski formula also shows itself to be equally applicable to the case of liquids over the whole range of temperature tried.

7. Polarization of the Scattered Light.

It should be noted that, according to Einstein's investigation, the light scattered in a direction transverse to the primary beam should be completely polarized. Actually, however, this is not the case. The imperfectness of the polarization of the light scattered by gases was first discovered by Strutt (the present Lord Rayleigh), and measurements of the magnitude of the effect have been made by a photographic method by him * and by Cabannes † and also by Gans ‡. The imperfect polarization can be detected visually even in the case of dust-free air at atmospheric pressure §, and with the gases at high pressure, the increased intensity enables *visual measurements* to be carried out. In the case of ether vapour, the effect is very feeble, the polarization in the transversely scattered light being nearly complete (about 98.5 per cent.), but the great intensity of the scattered light enables *visual measurements* to be carried out, and it is found that with increasing density of the vapour, the percentage of polarization does not appreciably change. In the case of the liquid, specially interesting effects are observed which will be dealt with in a separate paper.

Cabannes || has shown that owing to the imperfect polarization, the intensity of the transversely scattered light is increased and is greater than that given by the Rayleigh law in the ratio $\frac{6(1+\rho)}{6-7\rho}$, where ρ is the ratio of the weaker to the stronger component of polarization. It is found that the Einstein-Smoluchowski formula should be modified by a similar correcting factor in order to give results in agreement with experiment. The correction becomes very important when ρ is large.

* Proc. Roy. Soc. xciv. p. 453 (1918).

† *Ann. de Physique*, xv. pp. 1-150.

‡ *Ann. der Physik*, lxv. p. 97 (1921).

§ 'Nature,' Jan. 19, 1922.

|| *Loc. cit.*

8. *Relation of Molecular Scattering to Critical Opalescence.*

As we have already seen, the Einstein-Smoluchowski formula shows that there is a perfect continuity between the comparatively feeble light-scattering shown by gases and vapours under ordinary conditions and the extremely large scattering or opalescence which develops as the critical state is approached. At the critical point itself, the compressibility of the substance is infinite, and it follows that the Einstein-Smoluchowski formula gives an infinite value for the scattering power. This is obviously inadmissible, and Einstein* himself has pointed out that for a *very minute* region at and round the critical point, the neglect of second-order terms in the expression for the work done in altering the density is not permissible and the formula requires modification. This point has, however, not much importance for our present purpose, as the range of temperature over which the neglect of the second-order terms is not permissible is exceedingly small. It may be mentioned that the matter has been further discussed by Ornstein and Zernike†, who have proposed an amended formula applicable in the immediate neighbourhood of the critical point which leads to a finite value for the scattering at this point. The bearing of Ornstein and Zernike's results on the phenomena observed with ether will be dealt with separately.

9. *The Case of Carbon Dioxide and the permanent gases.*

The experimental confirmation of the Einstein-Smoluchowski formula for the case of ether vapour, and also in the case of various ordinary liquids, shows that its theoretical basis is thoroughly firm and that the formula may be justly expected to apply equally well in the case of other gases and vapours. It is therefore very important that the case of carbon dioxide and the permanent gases, *e. g.* oxygen, nitrogen, argon, &c., should be thoroughly investigated. The scattering power of saturated carbon dioxide vapour at 21° C. (that is, ten degrees below the critical temperature) has been determined by the present Lord Rayleigh, and found to be 102 times that of the gas at atmospheric pressure. The compressibility of carbon dioxide at this temperature is very great, and the Einstein-Smoluchowski formula shows that the scattering power of saturated carbon dioxide at 21° C. should have been about 855 times that of the gas at atmospheric pressure. The observed result thus apparently supports the Rayleigh law of scattering (the density of carbon dioxide at this temperature being about

* *Ann. der Physik*, xxxiii. p. 1275 (1910).

† *Proc. Amsterdam*, xvii. p. 793 (1914).

110 times the density of atmospheric pressures), and not the Einstein-Smoluchowski formula. The experimental result is however open to question, as Rayleigh mentions that his observation tube had a leak, and the density of the gas was therefore probably much less than that corresponding to the saturation pressure. Some observations made in a Cailletet tube containing CO_2 liquid and vapour by the authors show that both carbon dioxide liquid and vapour scatter light very strongly at and for a few degrees below the critical temperature, but the scattering power falls off very quickly with decreasing temperature. It is hoped to carry out a series of measurements at different temperatures with improved apparatus, and to obtain data in order decisively to settle the question whether the Einstein-Smoluchowski formula does really break down for carbon dioxide. Probably standing in very close relation to this is the fact that has been observed by Kammerlingh Onnes and his co-workers at the Leiden Laboratory, that pure oxygen, nitrogen*, and argon do not show the phenomenon of critical opalescence. It is obviously of the greatest importance to investigate whether in these cases the Einstein-Smoluchowski formula is applicable or not.

Till further data are available, it is probably not safe to venture an opinion, but it seems clear that the applicability of the thermodynamic reasoning of Einstein and Smoluchowski stands on an unchallengeable basis at least at ordinary temperatures and so far as gases and liquids are concerned. It will be noticed that the formula was derived on the basis of the classical theory of light in which it is assumed to consist of some form of continuous wave-propagation. In view of recent work in various modern fields of physics, and the known failure of the classical theory in explaining the facts regarding the emission and absorption of light, the question arises whether we are justified in assuming that the classical wave theory is necessarily capable of giving a strict quantitative explanation of the facts regarding the molecular scattering of light? Is it not possible that in the case of substances whose molecules have a relatively small light-scattering power, the infinite sub-divisibility of the energy of the incident waves which the classical theory assumes might break down? Then again is it not possible that the statistical-mechanical considerations on which the validity of Boltzmann's principle rests might require modification in the sense of the quantum theory, particularly in dealing with fluids at low temperatures? The answer to these questions can only be given when a more thorough experimental investigation of the facts of molecular

* Proc. Amsterdam Academy, xviii. p. 950 (1915).

scattering in dense vapours has been carried out. Such investigation has been undertaken by the authors, and it is hoped that before long the necessary data will be available.

10. *Summary.*

The paper considers the problem of the molecular scattering of light in dense vapours and gases *not* obeying Boyle's law. The following are the principal results :—

(1) It is shown by a discussion that the Rayleigh law of scattering, which is based on the assumption of a random distribution of the molecules in space, should not be applicable in these cases.

(2) Assuming the non-random distribution of the molecules in space to be given by Boltzmann's theorem, a calculation is made of the scattering power of the medium. The result obtained is interpreted with the aid of the virial equation, and it is shown that the scattering power per unit volume is proportional to the absolute temperature, to the square of the density of the substance, and to its compressibility. If the gas obeys Boyle's law, the expression reduces to the Rayleigh law.

(3) The result thus deduced directly from the principles of the kinetic theory agrees with the general formula derived from the thermodynamical theory of density fluctuations, developed by Einstein and Smoluchowski, of which a brief account is given.

(4) Experiments carried out with ether vapour and liquid over a large range of temperature both below and above the critical point completely confirm the Einstein-Smoluchowski formula for this substance.

(5) The corrections of the formula necessary in view of the imperfectness of the polarization of the transversely scattered light, and also in the immediate neighbourhood of the critical point when the compressibility becomes excessively great, are indicated.

(6) The cases of carbon dioxide and of the permanent gases are referred to and the possible significance of the results obtained in their cases is discussed.

Calcutta, India.

April 22nd, 1922.

Note added in proof (6th August) : Since the paper was sent in, experiments on the light-scattering in the vapours of benzene and pentane at different temperatures and also in carbon dioxide at high pressure contained in sealed bulbs have been carried out, and these definitely confirm the Einstein-Smoluchowski formula and show that the Rayleigh law of scattering is not valid except in gases obeying Boyle's law.

IX. *On the Anomaly of Strong Electrolytes with special Reference to the Theories of J. C. Ghosh.* By HENRY J. S. SAND, D.Sc., Ph.D., F.I.C.; Sir John Cass Technical Institute, London *.

Synopsis:—PART I. Introduction.—Application of Boltzmann's theorem to obtain an estimate of the degree of association of a completely ionized electrolyte immersed in a medium of uniform dielectric constant.—Application of Born & Landé's formula to obtain an estimate of the probability that an ion obeys the inverse square law.—Ghosh's virial formula.—Thermodynamical deduction of an equation for the heat of dilution of an electrolyte whose osmotic pressure obeys a law such as that of Ghosh or Milner.—Test of Ghosh's and of Milner's osmotic pressure formulæ by experimental results. PART II. Ghosh's theory of electrolytic conductivity.—Adjustment of the subsidiary hypotheses so that they yield Ghosh's conductivity formula.—Discussion of constancy of conductivity under varying electrical conditions in its relation to a theory of complete dissociation with uniform dielectric constant of the medium.—Rejection of the hypothesis of uniform dielectric medium, reference to similar conclusion by Milner.—Discussion of the rôle of molecules of solvent and of solvated ions.—Test of Ghosh's conductivity formula by experimental results, effect of substituting Milner's virial values into Ghosh's formula.

PART I.

THE problem of the anomaly of strong electrolytes has for the last thirty years or more, been one of the most baffling in physical chemistry. Some years ago J. C. Ghosh† put forward a theory which at the time appeared to go a long way towards the complete solution of this problem. The theory is based on the fundamental assumption that the solutions of strong electrolytes are completely ionized at all dilutions and that the ions attract each other according to the inverse square law as point charges placed in a continuous medium having the dielectric constant of the solvent. A very large amount of experimental evidence is adduced in support of the formulæ put forward. To arrive at these, Ghosh introduces a number of subsidiary hypotheses which would have to be proved to make the theory complete. The same formulæ are claimed to govern the variations of molecular conductivity with dilution in the case of all electrolytes of similar type, and these formulæ contain only

* Communicated by the Author.

† Chem. Soc. Journ. cxiii. p. 449; *ibid.* p. 627; *ibid.* p. 707; *ibid.* p. 790 (1918).

constants that are independent of the conductivity measurements themselves. The validity of this claim was disputed by J. R. Partington *, who also criticised the theory in other respects. A much more serious objection was raised by D. L. Chapman and H. J. George †, who pointed to the large number of subsidiary hypotheses and showed that one of Ghosh's principal formulæ was in contradiction with the hypothesis stated. This fact had been noticed by me about nine months previous to the publication of Chapman and George's note. On referring the matter to Dr. Ghosh, I was informed that the formulæ were modelled on the well-known equation of state of Dieterici ‡. I have since that time been engaged in a careful study of Ghosh's theory in the hope that it might be possible to vindicate it completely by a slight adjustment of the subsidiary hypotheses and perhaps to establish these more firmly. As will be seen the hypotheses may be adjusted to fit the formulæ, and on the whole the hypotheses are strengthened thereby. The attempts, however, to establish these have not been successful, and the conclusion has been reached that it is necessary to abandon the hypothesis of a uniform dielectric medium. Since the present study was undertaken a considerable number of papers has been published dealing with Ghosh's theory §. As, however, these treat the matter from different points of view from those adopted in this paper, it will be sufficient to refer to them, where their conclusions touch those reached in the present instance.

*Degree of association of a completely ionized electrolyte
in a uniform dielectric medium.*

The fundamental assumption of the complete dissociation of strong electrolytes is not new. It has formed the basis of theoretical work by W. Sutherland ||, by S. R. Milner ¶, by P. Hertz **, by N. Bjerrum ††. A clear distinction between

* Trans. Faraday Soc. xv. pp. 110 & 162 (1919).

† Phil. Mag. xli. p. 799 (1921).

‡ Ann. Phys. [4] v. p. 51 (1901).

§ J. Kendall, Am. Chem. Soc. Journ. xlv. pp. 717-738 (1922); Sv. Arrhenius, Zeit. Phys. Chem. c. pp. 9-25 (1922); C. A. Kraus, Amer. Chem. Soc. Journ. xliii. p. 2514 (1921); H. Kallmann, Zeit. Phys. Chem. xcvi. p. 433 (1921); and others.

|| Phil. Mag. iii. p. 161 (1902); *ibid.* xii. p. 1 (1906); *ibid.* xiv. p. 1. (1908).

¶ Phil. Mag. xxiii. p. 551 (1912); *ibid.* xxv. p. 742 (1913); *ibid.* xxxv. pp. 214 & 352 (1918).

** Ann. d. Physik, xxxvii. p. 1 (1912).

†† Zeit. Elektrochem. xxiv. p. 321 (1918).

complete ionization and complete dissociation should be made. As the result of modern work on crystal structure the view has become very generally accepted that crystals of salts such as sodium chloride consist of ions which are held together by electrical forces. When such crystals are dissolved in water no reason is apparent why any other mode of combination than holds in the solid state should come into play, *i. e.* the substance would remain completely ionized. The question would, however, still be open whether any considerable fraction of oppositely charged ions would be held by their charges in such close proximity that they would form doublets which would be indistinguishable from molecules. If this were so, as we have every reason to believe is the case with salt molecules in the condition of vapour, most of the properties of the substance, such as its gaseous pressure and the absence of electrical conductivity under the action of moderate potential gradients, will be the same as those of an undissociated substance. We should therefore term it "undissociated," and yet it would be completely ionized inasmuch as the mutual attraction of the ions would obey comparatively simple electrical laws and its properties would follow from general considerations based on such laws.

The question can be quantitatively approached by means of a theorem of the dynamical theory of gases due to Boltzmann, which Milner has also made the basis of his work on the anomaly of strong electrolytes in the papers referred to. We employ the theorem in the form in which it is stated by Milner, *loc. cit.* 1912, p. 553, viz. if p_w and p'_w stand for the probabilities of the occurrence of configurations of which the potential energies are W_1 and W_2 respectively in a system of molecules where intermolecular forces exist and p, p' stand for the probabilities of the occurrence of the same configurations in the same system of molecules if there were no intermolecular forces, then :

$$\frac{p_w}{p'_w} = \frac{p}{p'} e^{-\frac{W_1 - W_2}{\omega}}, \quad \dots \dots \dots (1)$$

where ω stands for the most probable value of the kinetic energy of a molecule. If R is the gas constant, T the absolute temperature, and N the number of molecules in a mol (Avogadro's constant), then

$$\omega = \frac{RT}{N} \dots \dots \dots (2)$$

This theorem may be made the base of an approximate

calculation to determine to what extent the probability that oppositely charged ions should be found in close proximity to each other, is affected by their charges, if we confine our attention to one pair of ions. We imagine the volume available to be equal to the average volume occupied by a pair of ions in the solution and assume the space to be of spherical shape with one of the ions fixed in the centre. Further, we assume that in the absence of any attractive force between the two ions all positions in small volumes of equal size in the sphere are equally probable for the second ion.

Before proceeding further it will, however, be necessary to consider more carefully the law according to which ions in a solution attract each other. We shall provisionally assume a uniform dielectric constant of the medium as was done by Ghosh, returning to the discussion of this assumption later on. As regards a comprehensive law according to which ions attract each other, we have particularly the researches of M. Born and A. Landé on the compressibility of salt crystals to refer to*. On these Born bases a theory of ionic structure leading to an expression for the potential energy W of a pair of attracting ions, of the form :

$$W = -\frac{a}{r} - \frac{b}{r^5} + \frac{c}{r^9} \quad \dots \quad (3)$$

Herein r is the distance between the centres of the two ions ; the constant a has the value which would make the first term express the potential energy of the pair of ions if they were point charges, *i. e.*

$$a = \frac{E^2}{\epsilon}, \quad \dots \quad (4)$$

where E is the elementary ionic charge and ϵ the dielectric constant of the medium. The second term is small, and may be neglected so that we may make

$$b = 0, \quad \dots \quad (5)$$

and the third may be expressed in terms of the distance which the centres of the ions would have if they were in equilibrium. This distance, which equals approximately the sum of the ionic radii in the crystalline state, we indicate

* *Verh. d. D. Phys. Ges.* xix, p. 210 (1918); *ibid.* xx, p. 232 (1918).

by d_0 . Thus we have

$$\frac{dW}{dr} = \frac{a}{d_0^2} - 9 \frac{c}{d_0^{10}} = 0 \quad (r=d_0),$$

$$\text{or} \quad c = \frac{ad_0^8}{9} \dots \dots \dots (6)$$

Substituting (4), (5), and (6) into (3) we obtain

$$W = -\frac{E^2}{\epsilon r} + \frac{E^2 d_0^8}{9 \epsilon r^9} \dots \dots \dots (3a)$$

The diameters of various ions have values for which we may refer to a table given by W. L. Bragg *. For our present purpose it will be sufficient to take as a representative value say $d=3 \times 10^{-8}$ cm.

We now come to the consideration of a concrete case. We imagine the solution to be of tenth normal strength. In this case the average volume occupied by a pair of ions will be $\frac{10000}{N}$ c.c., N being Avogadro's number, and this

would be the volume of the sphere referred to above. The radius of such a sphere is 15.85×10^{-8} cm. If no forces existed between the ions, but the other conditions we have postulated held, we calculate for the ratio of the two probabilities (1) that the ions are in contact, that is that their centres have a distance $r_1=3 \times 10^{-8}$ cm., and (2) that the second ion is somewhere near the circumference of the sphere, say that the distance of its centre from the centre of the sphere is $r_2=14 \times 10^{-8}$, the value :

$$\frac{P}{P'} = \frac{3^2}{14^2} = 0.046. \quad \dots \dots \dots (7)$$

If, however, the ions attract each other according to Born and Landé's law (3a), we find their potential energies, making $d_0=3 \times 10^{-8}$ cm., $E=4.7 \times 10^{-10}$ e.s.u., $\epsilon=80$, to be according to equation (3a) respectively

$$W_1 = -8.1818 \times 10^{-14} \text{ erg}; \quad \dots \dots \dots (8)$$

$$W_2 = -1.9723 \times 10^{-14} \text{ erg}. \quad \dots \dots \dots (9)$$

Making $R=8.317 \times 10^7$ ergs per degree and mol, $T=17^\circ \text{C}.$ $=290^\circ \text{abs.}$, $N=6.16 \times 10^{23}$, and substituting the values given by (2), (7), (8), and (9) into Boltzmann's equation (1),

* Phil. Mag. xl. p. 179 (1920).

we now calculate for the relative probabilities of the two configurations considered the ratio :

$$P_w : P_w' = 0.225,$$

i. e., the probability that the centres of the ions are in contact, *i. e.* at a distance of 3×10^{-8} cm. is in spite of the attractive forces only a little more than one-fifth of the probability that they are at the limit assumed, *i. e.* at a distance of about 14×10^{-8} cm. from each other. In this case the probability that the second ion is present in a given small volume in contact with the first is only 4.9 times as great as that it is in an element of volume of the same size near the circumference of the sphere considered. By making $W_2 = 0$ we can calculate that in an unlimited space the probability of the second ion being in contact with the first in a given small volume is 8.1 times as great as that it is in a small volume of equal size at such places where the attraction is negligible. On the other hand, if we make $\epsilon = 1$, and give to T so high a value even as $T 1273^\circ$ corresponding to the case of NaCl vapour at 1000°C. , we find for the above ratio the value 3.4×10^{16} . From this we conclude that even for very large volumes, *i. e.* at low pressures, the probability of the ions being in close proximity is overwhelmingly much greater than that they would be free from each other, and we should expect NaCl vapour to behave as an undissociated substance even although we assume it to be completely ionized. The absence of dissociation in the sense generally understood can therefore in this case not be employed as an argument against complete ionization as has been done in a recent discussion (R. M. Caven, *Nature*, cviii. p. 210 (1921)).

Approximate range of simple inverse square law for attraction of ions.

Another matter which is of interest is to know to what extent a law such as that of Born and Landé invalidates the use of the inverse square law. A simple calculation yields the result that if the ions are distributed uniformly in a solution of $\frac{N}{10}$ strength the volume of that part of it, in which the potential calculated according to Born and Landé differs by more than one per cent. from the value given by the inverse square law, is only 1.67 per cent. of the total volume of the solution. If we wish to find the probability that the attraction in the case of a given pair of ions does

not show a greater deviation from the inverse square law than that mentioned above, we should have to allow for the fact that positions of proximity are more probable than others according to Boltzmann's law. Here again as above, we can only arrive at an approximation by considering one of the ions fixed at the centre of a sphere the volume of which is equal to the average volume available for the pair of ions in the solution and the other ion free to move in this sphere. Even in this comparatively simple case the calculation is long and troublesome and leads to the result that the probability that the potential of the pair of ions would differ by more than one per cent. from that following from the inverse square law is about 3.7 per cent.

We may summarize the preceding considerations by saying: On the assumption that the solvent separating ions has a constant specific inductive capacity equal to that of the liquid in bulk, the hypothesis of complete ionization in the case of salts such as sodium chloride is well established, electrical association say in N/10 solution would be small, and the preponderating proportion of ions would be subject to the inverse square law of electrical action.

Ghosh's virial formula. Heat of dilution of an electrolyte conforming to Milner's or Ghosh's osmotic pressure formula.

As already stated, Ghosh requires for the purpose of his theory to evaluate the work which must be done to remove the ions arising from say a mol of salt in solution, from the sphere of each other's action. Milner (*loc. cit.* 1912) has calculated this quantity on the basis of Boltzmann's theorem for a binary electrolyte subject to the assumptions we have made above. In the case of forces obeying the inverse square law, this function is the same as the negative value of the one introduced into theoretical physics by Clausius under the name of the virial, and Milner terms it the attractive virial of the solution. The calculation is an extremely long and difficult one. Milner has applied the result to calculate the osmotic pressure, and hence the lowering of freezing points of binary electrolytes by making use of the Clausius' Virial theorem, according to which pressure times volume equals two-thirds kinetic energy minus one-third attractive virial. Milner discusses the application of this theorem to the osmotic pressure of a solution and supplies a new proof based on thermodynamical reasoning (*loc. cit.* xxv. p. 747). This proof however, like the dynamical one of

Clausius, applies only to gases for it contains two assumptions which do not hold for liquids. First, the temperature-coefficient of the dielectric constant is assumed to be zero, and Milner himself draws attention to the fact that this does not hold for liquids. Secondly, it contains the assumption that the difference in internal energy brought about in a solution by dilution is the result solely of overcoming the electrical forces between the ions, and that therefore the cooling of the solution should be the exact equivalent of this work. It is, however, doubtful whether the process of dilution in the case of an electrolytic solution does not essentially combine with the cooling effect just referred to, a production of heat of a similar order of magnitude. The matter is most readily understood by proceeding in the opposite direction to that adopted by Milner.

For the virial W of a solution Milner deduces a result of the general form :

$$W = RT h f(h), \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where f is a function of h for which values may be obtained from a table supplied (p. 749, *loc. cit.*) and h is a simple function of the product $V^{1/3} T \epsilon$, V being the dilution (*i. e.* volume per mol solute), T the absolute temperature, and ϵ the dielectric constant. The result may therefore be still more simply expressed as

$$W = T \mathfrak{F}, \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where $\mathfrak{F}$ is a function of the product

$$\sigma = \epsilon V^{1/3} T, \quad . \quad . \quad . \quad . \quad . \quad (12)$$

ϵ being considered a function of T only. In conjunction with the Clausius' virial theorem, Milner's result (10) applied to two mols of ions thus yields the relation :

$$PV = 2RT - \frac{1}{3} RT h f(h), \quad . \quad . \quad . \quad . \quad (13)$$

or more simply according to (11),

$$PV = 2RT - \frac{1}{3} T \mathfrak{F}. \quad . \quad . \quad . \quad (13a)$$

As explained above Milner further assumes that

$$\frac{\partial U}{\partial V} = - \frac{\partial W}{\partial V}, \quad . \quad . \quad . \quad . \quad (14)$$

where U is the internal energy of the solution. The two

equations (13 a) and (14) combined are, however, compatible with the thermodynamical relation also utilized by Milner :

$$\frac{\partial U}{\partial V} = T \frac{\partial P}{\partial T} - P^* \quad . \quad . \quad . \quad (15)$$

only when $\frac{d\epsilon}{dT} = 0$, for, substituting the values for P and $\frac{\partial P}{\partial T}$, which follow from (13 a), into (15), and comparing the result with that following from equations (11) and (12) for $\frac{\partial W}{\partial V}$, we find after some transformations :

$$\frac{\partial U}{\partial V} = - \frac{\partial W}{\partial V} - \frac{T^2}{3V^{2/3}} \frac{d\tilde{\gamma}}{d\sigma} \frac{d\epsilon}{dT},$$

and ultimately :

$$\frac{\partial U}{\partial V} = - \frac{\partial W}{\partial V} \left(1 + \frac{T}{\epsilon} \frac{d\epsilon}{dT} \right), \quad . \quad . \quad . \quad (16)$$

in place of the relation (14), assumed by Milner, which it would thus become necessary to drop in any attempt to apply his result to solutions. By integrating equation (16) we obtain for the heat of dilution H to zero concentration, the result :

$$H = U - U_{\infty} = -W \left(1 + \frac{T}{\epsilon} \frac{d\epsilon}{dT} \right). \quad . \quad . \quad . \quad (17)$$

A test of this formula by available heat data does not lead to satisfactory agreement, and we conclude therefore that an expression for the osmotic pressure of a solution of the general form given by equation (13), in conjunction with (12), which, as will be seen shortly, is common both to Milner and Ghosh, can have only approximate validity.

* In a recent paper (Phil. Mag. xliii. p. 625 (1922)) B. Cavanagh criticises Milner's application of the virial theorem to solutions. He further remarks, evidently with reference to Milner's use of the above thermodynamical equation (15), "The demonstration is open to grave doubts, for it depends on treating the solute thermodynamically as an independent system whose external pressure is the osmotic pressure of the solution." This latter criticism can however not be admitted, for equation (15) is a direct consequence of the quite general Gibbs-

Helmholtz equation and the very general relation $\frac{\partial A}{\partial V} = -P$, where A is the free energy, P the osmotic pressure, and V the dilution of a solution containing a given amount of solute and separated from pure solvent by a semipermeable membrane.

Ghosh's Virial Expression.—Like Milner, Ghosh applies the Clausius virial theorem, but in place of the virial deduced on the basis of the kinetic theory makes use of an energy term of an altogether different kind. He assumes that a mean disposition of the oppositely charged ions exists in solution and, further, that this disposition conforms to some simple pattern in space, analogous to the arrangement of the atoms in a solid crystal. Thus, in the case of a univalent binary salt, the mean positions of the ions are supposed to form a cubic space lattice, the distance r between two

adjacent ions being calculated to be $r = \sqrt[3]{\frac{V}{2N}}$, where V

is the dilution and N Avogadro's number. In the case of salts such as barium chloride a disposition such as that of the atoms of a fluorspar crystal is assumed; the distance between a barium and a chlorine ion is calculated to be

$\frac{\sqrt{3}}{2}r$, where r has the same value as in the case of binary

salts. With salts such as magnesium sulphate adjacent ions are supposed to approach each other more closely than in the case of univalent salts, the distances in the latter and former cases standing in the ratio $\sqrt[3]{4}$. In every case Ghosh calculates the work that is necessary to separate adjacent ions constituting an original molecule from each other and multiplies the result by the number of original molecules in the solution. If we indicate this work per gram-molecule of solute by G , Ghosh obtains in the case of a univalent binary electrolyte

$$G = \frac{NE^2 \sqrt[3]{2N}}{\epsilon \sqrt[3]{V}} = \frac{\sqrt[3]{2}}{10} \frac{F^2}{\epsilon N^{2/3}} \sqrt[3]{C}, \quad \dots (18)$$

where N is Avogadro's constant, E the electronic charge, ϵ the dielectric constant, F Faraday's constant $9654 \times 3 \times 10^{10}$ e.s.u. per g-equiv., and C the concentration measured in mols per litre. For an electrolyte such as barium chloride the result is put forward :

$$G = \frac{3NE^2 2 \sqrt[3]{2N}}{\epsilon \sqrt[3]{3} \sqrt[3]{V}} \dots \dots \dots (19)$$

This result would, however, correspond to an arrangement in which the distance of the chlorine atoms from each other is the same as their distance from the barium atom and is about four per cent. smaller than the value following from the arrangement postulated by Ghosh. Ghosh also erroneously defines the quantity which we have indicated by G as the work which is necessary to separate completely the

ions constituting an original gram-molecule of solute, i.e. $n \times N$ ions, n being the number of ions into which a molecule dissociates. This definition does not, however, agree with the arrangements of ions assumed, G being considerably smaller in every case. Thus for the lattice postulated for a univalent binary electrolyte, the energy necessary to separate the ions has been calculated by Madelung* in connexion with other researches, and is nearly 75 per cent. greater than G . The discrepancy between the values of G assumed by Ghosh and the interpretation given to them has also been pointed out by Kraus†, and a value agreeing with that previously given by Madelung has been quite recently calculated by Kendall‡ for univalent binary electrolytes.

In further dealing with Ghosh's theory it is thus evident that we must drop altogether the idea of an actual arrangement of the ions in the solution like that of the assumed space lattices. Indeed, it is plain that if a literal interpretation were given to these space lattices, the electrolytic solution or parts of it, should have axes, that is definite directions in space in which its properties were different from those in other directions. Two alternatives appear to be open to us. We may either consider the quantities G to be purely empirical energy expressions which when substituted into the Clausius virial equation yield an expression for the osmotic pressure agreeing, as will be shown below, within certain ranges with deductions from experiment; or else we may adhere to the interpretation of G as the work necessary to separate completely one gram-molecule of ions. This could be done, for example, by assuming that groups of ions constituting an original molecule were arranged in the manner required by Ghosh's space lattices, but that these groups had a random distribution among themselves. The artificiality of such explanations may justly be urged as an objection to them, and before proceeding further along the lines opened up by such theories, the rôle of the dielectric to which reference will be made below will no doubt have to be more closely scrutinized. In the meantime we shall probably do best to consider Ghosh's space lattices merely as theoretical "distributions of reference" the axes of which may be placed in arbitrary directions and which serve to yield units of length that are empirically important in the presentation of the free energy and conductivity relations of an electrolytic solution.

* *Phys. Zeit.* xix. p. 524 (1918).

† *Loc. cit.*

‡ *Loc. cit.*

Comparison of the deductions from Ghosh's and Milner's osmotic pressure formulæ, with experimental results.

Ghosh's expression for osmotic pressure has the same general form as Milner's, which is represented by equations (13a) and (12), and the disagreement between equation (17) and experiment referred to above thus shows that both can at best only claim limited validity. This validity we now come to examine. A comparison between theory and experiment is best made by utilizing van't Hoff's factor i which is defined by

$$PV = iRT.$$

By the aid of this equation we find on making the virial in the Clausius theorem applied to an original mol of electrolyte respectively equal to $RThf'(h)$ according to Milner, or equal to G according to Ghosh, that according to Milner :

$$2-i = \frac{1}{3}hf'(h) ; \quad . \quad . \quad . \quad . \quad . \quad (20)$$

whereas according to Ghosh :

$$2-i = \frac{1}{3} \frac{G}{RT} . \quad . \quad . \quad . \quad . \quad (21)$$

This equation (21) yields for univalent binary electrolytes (on substituting the value (18) for G and making $\epsilon=87.5$ at 0° , $T=273^\circ$, $R=8.32 \times 10^7$ ergs per degree per mol)

$$2-i = 0.2446 \sqrt[3]{C},$$

C being the concentration in mols per litre.

The following Table I. shows in the second and third lines the values of $2-i$ at various concentrations calculated according to Milner and to Ghosh respectively, and in the fourth line the ratio between the two. It will be seen that at about $N/100$ concentration the two are practically identical, whereas at lower concentrations Milner's values are smaller, and at higher concentrations greater than those of Ghosh. Milner's table (p. 749, *loc. cit.*), giving values for $\frac{1}{3}hf'(h) = 2-i$ at varying concentrations, may also be applied to binary bivalent electrolytes such as CuSO_4 , for a study of Milner's expression for h shows that binary bivalent electrolytes should, according to the theory, have the same value for $2-i$ as univalent ones, if their concentration is one sixty-fourth of the concentration of the univalent electrolyte. For bivalent electrolytes Milner's virial is the same as Ghosh's function at a concentration of about 3.1 thousandth normal and is smaller at lower concentrations.

TABLE I.

Concentrations (moles per litre)	0.002	0.005	0.01	0.02	0.05	0.1	0.2	0.5
$2-i = \frac{1}{2}h/fh$, acc. to Milner.....	0.0245	0.038	0.053	0.074	0.115	0.162	0.224	...
$2-i = \frac{1}{2}G/RT$, acc. to Ghosh	0.031	0.042	0.0527	0.0664	0.0901	0.1135	0.1431	0.1942
Ratio ($2-i$) Milner to ($2-i$) Ghosh	0.78	0.89	0.89	1.034	1.255	1.40	1.51	...
Percentage error in $2-i$ for $\left\{ \begin{array}{l} 1/1000^{\circ} \\ \text{an observational error of } 1/10,000^{\circ} \end{array} \right\}$...	...	...	93	42	11	4	2	$\frac{1}{3}$
	84	29	9	4	1	0.4	...	...
($2-i$) Experimental mean acc. to Ghosh {	...	...	0.058 (9%)	0.072 (4%)	0.100 (12%)	0.120 (17.5%)	0.151 (14%)	0.195 (12%)
($2-i$) Experimental mean acc. to Noyes and Falk	...	...	0.063	0.075	0.113	0.135	0.163	0.196
($2-i$) for KOI (Adams)	0.032	0.039	0.057	0.078	0.112	0.159	...	...
($2-i$) for KNO ₃ (Adams)	0.033	0.042	0.063	0.092	0.152	0.213	...	...

TABLE II.

Values of $\frac{2-i}{\sqrt{C}}$ for KIO₃ calculated from experiments by Hall and Harkins.

Theoretical value according to Ghosh equal 0.2446.

Concentrations (moles per litre)	0.00274	0.00506	0.00803	0.01358	0.03244	0.06380
$\frac{2-i}{\sqrt{C}}$	0.386	0.322	0.386	0.383	0.419	0.506

As regards the experimental determination of $2-i$ we are restricted almost entirely to the results of cryoscopic measurements. Even here the results must be considered doubtful at low concentrations. Recent American workers have claimed an accuracy of $1/10000$ degree for their measurements. We give accordingly in the fifth and sixth lines of Table I. the percentage variations in $2-i$ that correspond to an observational error in the cryoscopic measurements of $1/1000$ and $1/10000$ degree respectively. It will be realized that the test as here applied is a severe one, and also that there is little purpose in applying it to concentrations much below one-hundredth normal. Starting from the assumption that the values of i are the same for all uni-univalent electrolytes, Ghosh has calculated the mean of the principal available data for halogen salts, and his results are given in line 7 of Table I. Underneath each figure is given the maximum percentage variation from this mean in the case of the mean of any one given salt. In line 8 are given similar results that had been previously tabulated by Noyes and Falk*. In line 9 are given some more recent values for $2-i$ for KCl determined by L. H. Adams, and in line 10 similar values for KNO_3 †. In all calculations the molecular lowering for water has been taken as 1.858 (degree, litre, mol).

In Table II. some results are given for $2-i/\sqrt[3]{C}$ which I have calculated from experiments by R. E. Hall and W. D. Harkins‡ on KIO_3 and which may be compared with the value 0.2446 following from Ghosh's formula. The conclusion to be drawn from these results is that there are considerable differences between the i values of various univalent binary electrolytes, but that in the case of the halogen salts, the differences are comparatively small and some of the values agree well with the formulæ of Milner and of Ghosh.

When we come to binary bivalent electrolytes the formula of Ghosh gives the result $(2-i) : \sqrt[3]{C} = 1.553$, and as already explained Milner's formula yields practically the same value for a concentration of about three thousandth normal. The table supplied by Milner does not give values for $2-i$ at higher concentrations, whereas at lower concentrations the above expression would be smaller than 1.553 .

In Table III. are given some values for $(2-i)/\sqrt[3]{C}$ for various salts, most of which have been calculated from data

* J. Amer. Chem. Soc. xxxii. p. 1027 (1910).

† *Ibid.* xxxvii. p. 481 (1915).

‡ *Ibid.* xxxviii. p. 2658 (1916).

TABLE III.

Values of $\frac{2-i}{\sqrt{C}}$ calculated from experimental data. Theoretical value according to Ghosh equal 1.553.

MgSO_4	$\left\{ \begin{array}{l} \text{conc.} \dots\dots\dots 0.00630 \\ \frac{2-i}{\sqrt{C}} \dots\dots\dots 2.16 \end{array} \right.$	0.01310	0.02688	0.04878	0.06566	0.2210	...
CdSO_4	$\left\{ \begin{array}{l} \text{conc.} \dots\dots\dots 0.000704 \\ \frac{2-i}{\sqrt{C}} \dots\dots\dots 2.20 \end{array} \right.$	0.001511	0.002685	...	...	...	...
CuSO_4	$\left\{ \begin{array}{l} \text{conc.} \dots\dots\dots 0.001521 \\ \frac{2-i}{\sqrt{C}} \dots\dots\dots 2.63 \end{array} \right.$	0.003441	0.01463	0.1051	0.2074	0.4034	0.8894
ZnSO_4	$\left\{ \begin{array}{l} \text{conc.} \dots\dots\dots 0.001695 \\ \frac{2-i}{\sqrt{C}} \dots\dots\dots 2.23 \end{array} \right.$	0.002850	0.01391	0.1278	0.3112	1.001	...
		2.52	2.37	1.59	1.35	0.99	...

TABLE IV.

Values of $\frac{3-i}{\sqrt{C}}$ calculated from various experiments. Theoretical value according to Ghosh equal 0.8475.

BaCl_2 acc. to Hall and Harkins	$\left\{ \begin{array}{l} \text{conc.} \dots\dots\dots 0.00273 \\ \frac{3-i}{\sqrt{C}} \dots\dots\dots 1.153 \end{array} \right.$	0.00534	0.01142	0.02982	0.06611	0.81186	...
CoCl_2 acc. to Hall and Harkins	$\left\{ \begin{array}{l} \text{conc.} \dots\dots\dots 0.00209 \\ \frac{3-i}{\sqrt{C}} \dots\dots\dots 1.107 \end{array} \right.$	0.01008	0.02251	0.05475	0.1266	0.2772	0.4217

Experimental Mean adopted by Ghosh for electrolytes of type BaCl_2	$\left\{ \begin{array}{l} \text{conc.} \dots\dots\dots \\ \frac{3-i}{\sqrt{C}} \dots\dots\dots \end{array} \right.$	...	...	0.02	0.05	0.10	...
		...	...	0.843	0.839	0.819	...

collected by G. N. Lewis and G. A. Linhart*. The experiments are mainly due to Hall and Harkins† and to Hausrath‡.

For ternary electrolytes such as BaCl_2 Ghosh's formula leads to the result $(3-i)/\sqrt[3]{C}=0.8475$. Values for this quantity are assembled in Table IV, which have been calculated from experiments by Hall and Harkins and also from numbers given by Ghosh as representative mean values for various electrolytes.

Most of the results in Tables III. and IV. can only be said to agree with Ghosh's formulæ as regards order of magnitude, though the agreement between the mean of experimental values calculated by Ghosh for ternary electrolytes like BaCl_2 and his formula is close.

For electrolytes such as K_2SO_4 the values for $(3-i)/\sqrt[3]{C}$ differ considerably from the number 0.8475. They vary from about 1.3 to 1.7.

In conclusion, the application of Ghosh's formula to ebullioscopic results must be referred to. Confining ourselves to aqueous solutions of univalent binary electrolytes and therefore making $T=373^\circ$, $\epsilon=52.6$, Ghosh's formula leads to $(2-i)/\sqrt[3]{C}=0.306$; whereas a selection of results calculated for the same quantity from various experiments was found to vary from about 0.18 to about 0.58.

We may summarize the conclusions to be drawn from the results given by saying that the figures do not support the contention that van't Hoff's factor is solely dependent on the influences we have considered, and it cannot be maintained that it has the same value for all equimolecular solutions of electrolytes of similar type. In the cases reviewed the values following for $(n-i)$ from Ghosh's formulæ agree in order of magnitude with the available experimental data. As regards mean values for univalent binary chlorides in aqueous solution, the agreement between $(2-i)$ calculated from cryoscopic measurements and the same quantity derived from Ghosh's formula is good. Particularly at higher concentrations the agreement is better than that attained by Milner's formula, and empirically Ghosh's formula will therefore probably be preferred to the more elaborate theoretical one of Milner.

* J. Amer. Chem. Soc. xli. p. 1951 (1919).

† *Ibid.* xxxviii. p. 2672 (1916).

‡ *Ann. Phys.* ix. p. 522 (1902).

X. *On the Problem of two Moving Charges in its connexion with the Atomic Theory.* By S. BOGUSŁAWSKI, Professor at Moscow University*.

I. *Motion of two Charges with Masses varying according to the Lorentz-Einstein Law.*

1. **T**HE investigations of A. Sommerfeld have shown that the variation of mass of an electron with its velocity explains the structure of spectral lines of hydrogen and helium. Thus the facts observed in spectroscopy have come to support the accuracy of the Lorentz-Einstein formula for the variation of mass with velocity.

On the other hand, C. G. Darwin † and A. Sommerfeld ‡ carried out a closer investigation of the orbits of electrons moving according to this law under the attraction of a fixed positive charge, which shows that in certain circumstances the electron ought to describe spiral trajectories round the positive nucleus. There is no experimental evidence in favour of these orbits, and there is a considerable amount of indirect evidence which leads one to believe that these orbits do not occur in reality. A purely formal explanation of the unreality of those orbits is readily supplied by the quantum theory, the angular momentum for them being so small as not to be admitted by Bohr's theory of atoms. But it is doubtful how far this explanation may be considered as sufficient. It may be claimed that the quantum theory selects only those orbits which are in a certain sense stable, and does not deny altogether the possibility of other unstable orbits. From the latter point of view, the investigations of C. G. Darwin and A. Sommerfeld dealing with spiral orbits have not lost their interest.

There is a point in these investigations which makes them appear incomplete, and their result not so convincing as is desirable: I mean the fact that both these authors consider the central charge as fixed in space. This supposition gives a result of a high degree of accuracy so long as the mass of the central charge is large compared with the mass of the charge revolving round it. But this last condition ceases to be fulfilled from a certain moment while the charge

* Communicated by the Author.

† C. G. Darwin, *Phil. Mag.* (6) vol. xxv. p. 201 (1913).

‡ A. Sommerfeld, *Ann. d. Phys.* 1916; also 'Atombau und Spektrallinien,' 2nd edition, p. 324 (1921).

is approaching the central kernel along a spiral trajectory. As the distance between them decreases, the velocity and the mass of the moving charge must both increase so that the latter may become comparable with that of the central charge. It is true that this will only occur when the distance between the charges is comparable with the diameter of the electron. In this case our knowledge of the dynamics of any masses becomes uncertain. As far as experience on scattering of α -rays goes, Coulomb's law seems to hold good even for distances of this order of magnitude. At lower distances, however, this law probably ceases to be true, as is shown by later experiments of Sir E. Rutherford on the production of H-rays by collision of α -particles with atoms. For this reason it is doubtful whether theoretical orbits which, like the spiral ones, approach very closely the central nucleus give an accurate description of real facts. But all the same, even if the theory does not here find immediate application, the theoretical investigation of an idealized problem does not lose its interest, and may help in some way to find the correct solution. From this standpoint, I thought it useful to study the motion of two charges whose masses vary according to the law given by the theory of relativity. I could not find out whether anybody has already studied this problem. But owing to the state of things in our country, we were so badly supplied with literature that possibly I am ill-informed.

The result of this study will be to confirm the results previously obtained by C. G. Darwin and A. Sommerfeld, in the sense that by taking into account the motion of the central nucleus, we still obtain spiral trajectories in relative motion of the two charges when the relative angular momentum is sufficiently small.

2. To find the solution of our problem we shall apply the method of the differential equation of Hamilton-Jacobi. This method seems to be the most appropriate for purposes of atom dynamics, because it gives the result in a form to which the principles of the quantum theory can be immediately applied. But also in cases where no use of quantum theory is made, the method can be recommended for its compactness.

Let e_1 and e_2 denote two charges, whose masses for infinitely small velocities are respectively m_1 and m_2 . Let x_1, y_1, z_1 be the coordinates of the first charge; x_2, y_2, z_2

those of the second. We put, according to the general use,

$$\beta_1^2 = \frac{1}{c^2} (\dot{x}_1^2 + \dot{y}_1^2 + \dot{z}_1^2), \quad \beta_2^2 = \frac{1}{c^2} (\dot{x}_2^2 + \dot{y}_2^2 + \dot{z}_2^2),$$

where c is the velocity of light.

The Lagrangean function of our problem is

$$L = -m_1 c^2 \sqrt{1 - \beta_1^2} - m_2 c^2 \sqrt{1 - \beta_2^2} - \frac{e_1 e_2}{r} \quad . \quad . \quad (1)$$

with

$$r^2 = (x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2.$$

The impulses of the two masses will be

$$p_{x_1} = \frac{\partial L}{\partial \dot{x}_1} = \frac{m_1 \dot{x}_1}{\sqrt{1 - \beta_1^2}}, \dots, \quad p_{x_2} = \frac{\partial L}{\partial \dot{x}_2} = \frac{m_2 \dot{x}_2}{\sqrt{1 - \beta_2^2}}, \dots \quad (2)$$

The Hamiltonian function of the problem which expresses the total energy of the system is

$$H = \Sigma \dot{x}_1 p_{x_1} + \Sigma \dot{x}_2 p_{x_2} - L, \quad . \quad . \quad . \quad (3)$$

where the symbol Σ means a summation over the three coordinates. Making use of (1) and (2), and expressing the velocities in terms of the impulses, we bring (3) in the form

$$H = c \sqrt{m_1^2 c^2 + \Sigma p_{x_1}^2} + c \sqrt{m_2^2 c^2 + \Sigma p_{x_2}^2} + \frac{e_1 e_2}{r}. \quad . \quad (4)$$

If, now, we suppose $p_{x_1}, \dots, p_{x_2}$ to be the six partial differential coefficients of a function W corresponding to the six independent variables $x_1, \dots, z_2$, and put the right side of (4) equal to a constant α_1' , we shall obtain the partial differential equation of Hamilton-Jacobi, on whose solution depends the solution of our problem. The constant α_1' is the total energy of our system, consisting of the kinetic energy of both masses, their mutual potential energy as expressed by the last term in (4), and of the internal energy stored in both masses, which according to the theory of relativity amounts to $m_1 c^2$ and $m_2 c^2$ respectively for the two masses.

Transforming the differential equation in order to get rid of the irrationalities, we can write it in the form

$$\begin{aligned} c^4 (m_1^2 - m_2^2)^2 + \Sigma p_{x_1}^2 - \Sigma p_{x_2}^2 + 2c^2 (m_1^2 - m_2^2) (\Sigma p_{x_1}^2 - \Sigma p_{x_2}^2) \\ + \frac{1}{c^2} \left(\alpha_1' - \frac{e_1 e_2}{r} \right)^2 \left\{ \frac{1}{c^2} \left(\alpha_1' - \frac{e_1 e_2}{r} \right)^2 \right. \\ \left. - 2(m_1^2 + m_2^2)c^2 - 2(\Sigma p_{x_1}^2 + \Sigma p_{x_2}^2) \right\} = 0. \quad . \quad (5) \end{aligned}$$

This is the equation that we have now to solve.

3. We introduce new variables by putting

$$\left. \begin{aligned} x &= x_1 - x_2, & \xi &= x_1 + x_2, \\ y &= y_1 - y_2, & \eta &= y_1 + y_2, \\ z &= z_1 - z_2, & \zeta &= z_1 + z_2, \end{aligned} \right\} \dots \dots (6)$$

where x, y, z are obviously the relative coordinates of the first mass as referred to the second. The partial differential coefficients $p_{x_1}, \dots, p_{z_2}$ will then be expressed in terms of the new ones $p_x, \dots, p_\zeta$ as follows:—

$$\left. \begin{aligned} p_{x_1} &= p_\xi + p_x, & p_{x_2} &= p_\xi - p_x, \\ p_{y_1} &= p_\eta + p_y, & p_{y_2} &= p_\eta - p_y, \\ p_{z_1} &= p_\zeta + p_z, & p_{z_2} &= p_\zeta - p_z. \end{aligned} \right\} \dots \dots (7)$$

Solving these equations, we shall have

$$p_\xi = \frac{1}{2}(p_{x_1} + p_{x_2}), \quad p_x = \frac{1}{2}(p_{x_1} - p_{x_2}); \dots \dots (8)$$

and similarly for the two other axes.

It follows from (7)

$$\left. \begin{aligned} \Sigma p_{x_1}^2 + \Sigma p_{x_2}^2 &= 2(\Sigma p_\xi^2 + \Sigma p_x^2), \\ \Sigma p_{x_1}^2 - \Sigma p_{x_2}^2 &= 4(p_\xi p_x + p_\eta p_y + p_\zeta p_z). \end{aligned} \right\} \dots \dots (9)$$

Since the equation (5) does not contain explicitly the variables ξ, η, ζ , the distance r depending only on x, y, z , the differential coefficients p_ξ, p_η, p_ζ may be regarded as constants. The physical meaning of this is, as is shown by (8) and (2), that the total momentum of the system is constant during the motion.

Substituting (9) in (5), we obtain a quadratic differential equation in the three variables x, y, z . This equation describes the relative motion of the two masses.

We shall confine our investigation to the case when the total momentum is equal to zero, and put accordingly

$$p_\xi = p_\eta = p_\zeta = 0. \dots \dots (10)$$

Then the second and third terms of equation (5) dis-

appear, and the result is

$$\Sigma p_x^2 = \frac{1}{4c^2} \left(\alpha_1' - \frac{e_1 e_2}{r} \right)^2 - \frac{1}{2} (m_1^2 + m_2^2) c^2 + \frac{c^6 (m_1^2 - m_2^2)^2}{4 \left(\alpha_1' - \frac{e_1 e_2}{r} \right)^2}. \quad (11)$$

It is easily seen that the relative motion is a plane one. Therefore we can describe the motion by using polar co-ordinates in the plane of relative motion. We can do that, for instance, by choosing the z -axis perpendicular to the plane of motion and by putting further

$$x = r \cos \phi, \quad y = r \sin \phi.$$

Then we have

$$\Sigma p_x^2 = p_r^2 + \frac{p_\phi^2}{r^2}, \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where p_r and p_ϕ are the partial differential coefficients of the function W corresponding to the variables r and ϕ .

Substituting (10) into (11), we see that our equation does not contain explicitly ϕ , and that accordingly p_ϕ may be considered as a constant. This means physically that the relative angular momentum is constant throughout the motion. We put

$$p_\phi = \alpha_2.$$

Equation (11) becomes

$$p_r^2 = \frac{1}{4c^2} \left(\alpha_1' - \frac{e_1 e_2}{r} \right)^2 - \frac{1}{2} (m_1^2 + m_2^2) c^2 + \frac{c^6 (m_1^2 - m_2^2)^2}{4 \left(\alpha_1' - \frac{e_1 e_2}{r} \right)^2} - \frac{\alpha_2^2}{r^2}. \quad (13)$$

Having thus found the value of p_r in terms of r only, and knowing p_ϕ to be constant, we can write the solution of our equation.

For brevity's sake we shall write $P(1/r)$ for the right side of (13). Then the solution is

$$W = \int \sqrt{P(1/r)} dr + \alpha_2 \phi. \quad . \quad . \quad . \quad . \quad (14)$$

The equation of the orbit being

$$\frac{\partial W}{\partial \alpha_2} = \beta_2,$$

where β_2 is another constant, we obtain from (14) the equation of the orbit in relative motion in the form

$$\phi - \beta_2 = - \int \frac{\alpha_2 d(1/r)}{\sqrt{P(1/r)}}, \quad \dots \quad (15)$$

which we have now to discuss. We shall choose the particular values of β_2 so as to make an apex of the curve, if there is any, to correspond to $\phi = 0$.

4. We shall put

$$\alpha_1' = \alpha_1 + (m_1 + m_2)e^2,$$

where α_1 is a constant expressing the sum of the kinetic and potential energies of our system.

If we confine our attention to cases which are of greater practical interest, we may consider the kinetic energy as small compared with the energy accumulated in the masses when at rest. This comes to supposing that

$$\frac{\alpha_1 - \frac{e_1 e_2}{r}}{(m_1 + m_2)c^2} \quad \dots \quad (16)$$

is small compared with unity. If the expression (13) for $P(1/r)$ is developed in powers of (16), and the powers higher than the second are neglected, then it assumes the form

$$P(1/r) = \frac{2m_1 m_2}{m_1 + m_2} \left(\alpha_1 - \frac{e_1 e_2}{r} \right) + \frac{1}{c^2} \left[1 - \frac{3m_1 m_2}{(m_1 + m_2)^2} \right] \left(\alpha_1 - \frac{e_1 e_2}{r} \right)^2 - \frac{\alpha_2^2}{r^2} \quad \dots \quad (17)$$

This expression being quadratic in $1/r$, the integral in (15) is of elementary kind, and the form of the orbit can be easily discussed.

If we put

$$\left. \begin{aligned} \eta^2 - 1 &= \frac{2\alpha_1(m_1 + m_2) \left[1 + \frac{\alpha_1}{2c^2} \left(\frac{m_1^2 - m_1m_2 + m_2^2}{m_1^2m_2 + m_1m_2^2} \right) \right] \left\{ \alpha_2^2 - \left(\frac{e_1e_2}{c} \right)^2 \left[1 - \frac{3m_1m_2}{(m_1 + m_2)^2} \right] \right\}}{m_1m_2e_1^2e_2^2 \left[1 + \frac{\alpha_1}{c^2} \left(\frac{m_1^2 - m_1m_2 + m_2^2}{m_1^2m_2 + m_1m_2^2} \right) \right]^2}, \\ p &= - \frac{\alpha_2^2 - \left(\frac{e_1e_2}{c} \right)^2 \left[1 - \frac{3m_1m_2}{(m_1 + m_2)^2} \right]}{m_1m_2e_1e_2 \left[1 + \frac{\alpha_1}{c^2} \left(\frac{m_1^2 - m_1m_2 + m_2^2}{m_1^2m_2 + m_1m_2^2} \right) \right]}, \\ \gamma^2 &= 1 - \left(\frac{e_1e_2}{\alpha_2c} \right)^2 \left[1 - \frac{3m_1m_2}{(m_1 + m_2)^2} \right], \end{aligned} \right\} \quad (18)$$

then for positive values of γ^2 equation (15) will take the form

$$\frac{p}{r} = 1 + \eta \cos(\gamma\phi). \quad (19)$$

If, however, γ^2 is negative, we shall have to put

$$\gamma = i\delta,$$

and shall obtain instead of (19)

$$\frac{p}{r} = 1 - \eta \cosh(\delta\phi). \quad (20)$$

The intermediate case $\gamma^2 = 0$ leads to an algebraic quadratic equation between r and ϕ , which need not be written down, because the properties of the corresponding orbit as the intermediate orbit between the orbits (19) and (20) are sufficiently obvious.

We see that the equations (19) and (20) are exactly the same as in the case of a fixed centre of force. The whole difference lies in the values of the three constants η , p , and γ , which are modified by our supposition that both masses are moving under their mutual attraction or repulsion. We obtain the formulæ for a fixed mass m_2 by putting $\frac{m_2}{m_1} = \infty$.

If, on the other hand, we put in (18) $c = \infty$, we obtain the formulæ of the classic problem of two bodies. In this case we have $\gamma = 1$, and the relative trajectories are conics.

It is hardly necessary to discuss the equations (19) and (20) in full detail.

The curve (19) may be described as generated by the superposition of a motion in a conic and a rotation of the perihelion. The constant γ^2 being smaller than unity, the rotation is in the same direction in which the mass moves along the conic.

The curve (20) is in most cases a spiral (and so is the intermediate curve $\gamma=0$). If $\eta > 1$, both ends of the curve are spirals winding round the origin. This can obviously happen only in the case of attraction, as it requires that α_1 should be negative. The value of p in (20) being negative, the curve is real for all values of ϕ between $-\infty$ and $+\infty$. But if $\eta < 1$, only one end of the curve is a spiral if e_1 and e_2 are of different sign, the other one stretching to infinity. In this case α_1 must be positive, which does not lay any restriction on the signs of the charges. If there is attraction, p is negative and the curve is included between the asymptote $\phi = \pm \frac{1}{\delta} \operatorname{arccosh} \frac{1}{\eta}$ and $\phi = \pm \infty$, where the signs have to be taken either both positive or both negative. In the case of repulsion, p is positive and the curve is included between the two asymptotes $\phi = \frac{1}{\delta} \operatorname{arccosh} \frac{1}{\eta}$. This time it is not a spiral, but a distorted branch of an hyperbola.

The critical value of the angular momentum corresponding to $\gamma=0$ is in our case

$$\alpha_2^2 = \left(\frac{e_1 e_2}{c}\right)^2 \left[1 - \frac{3m_1 m_2}{(m_1 + m_2)^2}\right] \quad . \quad . \quad . \quad (21)$$

compared with

$$\alpha_2^2 = \left(\frac{e_1 e_2}{c}\right)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

in the case of a fixed centre. Thus for a moving centre the critical value is smaller than for a fixed one. The effect is largest for $m_1 = m_2$, (21) giving then a twice smaller value than (22). For a hydrogen atom the effect is a negligible one, roughly 1 in 1200; for a helium ion, nearly 1 in 5000.

We come to the conclusion that on the theory of relativity the relative motion of two charges is of much the same kind as the motion round a fixed centre of attraction. In cases of practical importance the quantitative difference between them is only small.

But we must not forget that the conclusions of this paragraph are only valid so long as the kinetic energy is small compared with the energy stored in the masses. This means that our equations give an approximately accurate description of those parts of the orbits where r is not too small. Thus equation (20) describes accurately only the outer parts of spiral trajectories. Knowing nothing about the inner part of it, we cannot even decide whether for given value of α_2 the real orbit will be a spiral one or not. The critical value (21) determines only the analytical form of the equation for the outer part, but, as we shall see in the next paragraph, does not provide a criterion which would allow us to decide whether the orbit is a spiral one or not.

5. The investigation of the last paragraph was based on the assumption that the sum of the kinetic and potential energies of the system is small compared with the energy stored in the masses.

The solution of the problem for the exact value (13) of $P(1/r)$ is far more difficult. But if we do not attempt to discuss the form of the trajectories in full detail, but limit our attention to the question whether spiral trajectories still occur and under what condition, the problem is a very simple one, and the form of $P(1/r)$ provides us all the information that we want. According to (13), $P(1/r)$ must be positive for any real motion. Spiral trajectories will accordingly be possible whenever the right side of (13) is positive for infinitely decreasing values of r . In other words, we may have spiral trajectories if the coefficient of $1/r^2$ is positive, but not if it is negative. This leads again to a critical value for α_2 . The coefficient of $1/r^2$ being $\left(\frac{e_1 e_2}{2c}\right)^2 - \alpha_2^2$, the condition for spiral trajectories is

$$\alpha_2^2 < \left(\frac{e_1 e_2}{2c}\right)^2. \quad . \quad . \quad . \quad . \quad . \quad (23)$$

This is the value which we obtained in the previous paragraph for the case of equal masses, using an approximate method.

The physical meaning of the constant α_2 may not be obvious from the above formulæ. We can easily show that it really is the quantity which must be called the angular momentum of relative motion on the Einstein theory. It follows from (7), (10), and (12),

$$\Sigma p_{x_1}^2 = \Sigma p_{x_2}^2 = \Sigma p_x^2 = p_r^2 + \frac{p_\phi^2}{r^2}.$$

Substituting this into (4), we have one of the canonical differential equations :

$$\dot{\phi} = \frac{\partial H}{\partial p_{\phi}} = \frac{cp_{\phi}}{r^2} \left[\frac{1}{\sqrt{m_1^2 c^2 + \Sigma p_{x_1}^2}} + \frac{1}{\sqrt{m_2^2 c^2 + \Sigma p_{x_2}^2}} \right].$$

Putting $p_{\phi} = \alpha_2$, and using (2), we find

$$\alpha_2 = \frac{r^2 \dot{\phi}}{\frac{\sqrt{1-\beta_1^2}}{m_1} + \frac{\sqrt{1-\beta_2^2}}{m_2}}.$$

As in the classical problem of two bodies, the rôle of the reciprocal value of the mass is played by the sum of the reciprocal values of the two masses, both expressed in terms of their velocities. Thus α_2 really deserves the name of the angular momentum of relative motion.

6. The results obtained in the previous pages may be summed up as follows :—

The Hamilton-Jacobi equation for two charges moving under mutual attraction or repulsion with masses varying according to Einstein's law can be easily solved, when the total momentum of the system is equal zero.

The exact solution of the equation shows that, if there is attraction, for small values of relative angular momentum the relative trajectory is a spiral, as in the case of fixed centre of attraction. The critical value of angular momentum is half of its value in the latter case.

The discussion of the exact solution in detail is not attempted. For practical purposes it is sufficient to discuss the approximate solution, which is obtained by supposing the kinetic energy of the system small compared with the energy stored in the masses. On this assumption the explicit equations of the trajectories are the same as for a fixed centre. Only the values of the constants in these equations are modified. The effect on the hydrogen or helium spectrum brought about by this modification is, however, so small that it could not be observed.

II. *Study of the mutual Magnetic Action of two Moving Charges.*

7. There is another problem which is in many ways related to the one studied above, and which can easily be solved by the same method. The atomic theory in its

simplest form takes no account of the magnetic forces arising from the mutual displacement of charges in the atom; in fact, these forces in an atom of hydrogen or in a helium ion are so small compared with electrostatic ones that they have to be neglected.

In atoms containing more than one electron these forces probably cannot be neglected. D. Roschdestvensky and G. Krutkow*, and independently myself, some two years ago came to the conclusion that these forces account for the doublets in the arc spectra of alkali metals. A. Sommerfeld†, in the 3rd edition of his excellent book 'Atombau und Spektrallinien,' gives a theory of doublets and triplets based on the same idea. But these are not the facts with which we propose to deal in the present paper.

As in the previous section, we are going to study the movement of a system consisting of only two charges; so that our result will bear only on the theory of the hydrogen atom and the helium ion. We intend to find out in what way the relative trajectories of two charges are modified by the magnetic field arising from their motion. We shall be able to compute the influence of these forces on the spectra emitted by such systems. However small this influence may be, it is not uninteresting from a theoretical point of view.

8. We must confine our attention to cases of *quasi-stationary* movement of the charges. This means that the changes in the state of the system are supposed to be so slow that we may neglect the time necessary for the propagation of the electromagnetic disturbance from one charge to the other. In atomic theory we are certainly entitled to do so. Then the Lagrangean function of our system has the form

$$L = \frac{m_1 v_1^2}{2} + \frac{m_2 v_2^2}{2} + \gamma(\dot{x}_1 \dot{x}_2 + \dot{y}_1 \dot{y}_2 + \dot{z}_1 \dot{z}_2) - c^2 \gamma, \quad (24)$$

where we put for brevity's sake

$$\frac{e_1 e_2}{c^2 r} = \gamma. \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

* D. Roschdestvensky, 'Verhandlungen des Optischen Instituts in Petersburg,' Berlin, 1921.

† A. Sommerfeld, 'Atombau und Spektrallinien,' Braunschweig, 1922.

The third term on the right side of (24) accounts for magnetic forces. We consider the masses as constant.

The momenta of the masses are :

$$\left. \begin{aligned} p_{x_1} &= \frac{\partial L}{\partial \dot{x}_1} = m_1 \dot{x}_1 + \gamma \dot{x}_2, \\ p_{x_2} &= \frac{\partial L}{\partial \dot{x}_2} = \gamma \dot{x}_1 + m_2 \dot{x}_2, \end{aligned} \right\} \dots \dots (26)$$

and similarly for the two other axes.

The Hamiltonian function as computed by (3) differs from the Lagrangean function (24) only by the sign of the last term. Solving (26), we find

$$\begin{aligned} \dot{x}_1 &= \frac{m_2 p_{x_1} - \gamma p_{x_2}}{m_1 m_2 - \gamma^2}, \\ \dot{x}_2 &= \frac{m_1 p_{x_2} - \gamma p_{x_1}}{m_1 m_2 - \gamma^2}. \end{aligned}$$

Substituting this and the analogous expressions of the remaining four components of velocities in the formula for the Hamiltonian function, we find

$$H = \frac{1}{m_1 m_2 - \gamma^2} \left\{ \frac{m_2}{2} (p_{x_1}^2 + p_{y_1}^2 + p_{z_1}^2) + \frac{m_1}{2} (p_{x_2}^2 + p_{y_2}^2 + p_{z_2}^2) - \gamma (p_{x_1} p_{x_2} + p_{y_1} p_{y_2} + p_{z_1} p_{z_2}) \right\} + c^2 \gamma. \quad (27)$$

Putting the right side equal to the total energy α_1 , we obtain the differential equation of Hamilton-Jacobi.

9. We proceed to solve this equation by the same method as we used in § 3. Using the variables (6) and the formulæ (7), we bring the equation to the form

$$\begin{aligned} \frac{1}{m_1 m_2 - \gamma^2} \left\{ \left(\frac{m_1 + m_2}{2} - \gamma \right) \Sigma p_{\xi}^2 + \left(\frac{m_1 + m_2}{2} + \gamma \right) \Sigma p_x^2 \right. \\ \left. + (m_2 - m_1) \Sigma p_x p_{\xi} \right\} + c^2 \gamma = \alpha_1. \quad (28) \end{aligned}$$

We see again that the total momentum whose components are p_{ξ} , p_{η} , p_{ζ} is constant throughout the motion.

If, again, we limit our attention to the case

$$p_{\xi} = p_{\eta} = p_{\zeta} = 0,$$

and introduce polar coordinates in the plane of relative motion, (28) takes the simpler form

$$\left(\frac{m_1+m_2}{2}+\gamma\right)\left(p_r^2-\frac{p_\phi^2}{r^2}\right)=(\alpha_1-c^2\gamma)(m_1m_2-\gamma^2). \quad (29)$$

For practical purposes we may consider γ as small compared with m_1 or m_2 . Indeed, we see from (25) that the absolute value of γ is the amount of mass which on the theory of relativity corresponds to the mutual potential energy of the charges. This amount is always small compared with the masses themselves. Thus we can further simplify (29) and obtain the equation

$$p_r^2 = \frac{2m_1m_2}{m_1+m_2} \left(\alpha_1 - \frac{e_1e_2}{r}\right) \left(1 - \frac{2e_1e_2}{(m_1+m_2)c^2} \cdot \frac{1}{r}\right) - \frac{\alpha_2^2}{r^2}. \quad (30)$$

Here we have substituted for γ its value (25) and put $p_\phi = \alpha_2$. Putting $S(1/r)$ for the right side of (30), we have the solution of the differential equation of Hamilton-Jacobi:

$$W = \int \sqrt{S(1/r)} dr + \alpha_2 \phi. \quad (31)$$

The equation of the orbit in relative motion is

$$\beta_2 = \alpha_2 \int \frac{d(1/r)}{\sqrt{S(1/r)}} + \phi. \quad (32)$$

Since $S(1/r)$ is again a quadratic function of $1/r$, the explicit form of the equation of the trajectory is again (19) or (20) if the value of β_2 in (32) is chosen so as to make an apex of the curve to correspond to $\phi=0$. The constants in these equations have the values

$$\left. \begin{aligned} \eta^2 - 1 &= \frac{2\alpha_1(m_1+m_2) \left[\alpha_2^2 - \frac{4m_1m_2e_1^2e_2^2}{(m_1+m_2)^2c^2} \right]}{m_1m_2e_1^2e_2^2 \left[1 + \frac{2\alpha_1}{(m_1+m_2)c^2} \right]^2}, \\ p &= - \frac{\alpha_2^2 - \frac{4m_1m_2e_1^2e_2^2}{(m_1+m_2)^2c^2}}{\frac{m_1m_2}{m_1+m_2}e_1e_2 \left[1 + \frac{2\alpha_1}{(m_1+m_2)c^2} \right]}, \\ \gamma &= \sqrt{1 - \frac{4m_1m_2e_1^2e_2^2}{\alpha_2^2(m_1+m_2)^2c^2}} \end{aligned} \right\} \quad (33)$$

But again, as in the former case, we must keep in mind that our formulæ apply only to orbits or to parts of orbits where the two charges do not come too close together. So if for a given very small value of α_2 , a part of the orbit can be with sufficient accuracy described by equation (20), we cannot conclude that this orbit will be a spiral throughout. The accurate equation (29) shows rather that spiral trajectories in this case are impossible. But we need not dwell on these details.

Formulæ (33) describe the disturbance of the motion caused by the magnetic field which it produces. They show that, for an originally elliptic orbit, both the greater semi-axis and the excentricity are slightly altered by the magnetic forces. And, what is more important, the orbit is no longer a closed curve, but there is a slow progression of apses, because γ differs from unity. All these disturbances are very small. It is easily seen from (33) that they are largest

for $m_1 = m_2$ and disappear as well for $\frac{m_1}{m_2} = 0$ as for $\frac{m_1}{m_2} = \infty$.

This result could be easily anticipated. Indeed, if one of the masses is large compared with the other, its velocity is small, and so is the magnetic field produced by its motion. The order of magnitude of the disturbances is the same as the order of the corrections to the relativity effect found in the first part of this paper. If m_1 is the mass of an electron and m_2 the mass of the nucleus of a hydrogen or helium atom, and we call x the order of the disturbance produced by the relativity variation of mass, then the order of the disturbances under consideration is $\frac{m_1 v}{m_2}$.

It is interesting to compare the last formulæ of the sets (18) and (33). If we measure by $1 - \gamma^2$ the rotation of apses, we see from (18) that the rotation produced by the relativity effect is decreased by $\frac{3m_1 m_2}{(m_1 + m_2)^2} \left(\frac{e_1 e_2}{\alpha_2 v} \right)^2$ when we take into account the motion of both masses. On the other hand, (33) shows that the effect of the magnetic forces is to increase it by $\frac{4}{3}$ of the same quantity.

10. From what has been stated already, we gather that the magnetic forces must cause a structure of spectral lines of the same kind as is produced by the relativity effect,

only on a scale $\frac{m_1}{m_2}$ times smaller. This ratio for a hydrogen atom being $1/1840$, the effect cannot be observed experimentally. We give a brief computation of its value. The quantum equations determining the values of α_1 and α_2 are:

$$2 \int_{r_1}^{r_2} \sqrt{S(1/r)} dr = n_1 h,$$

$$\int_0^{2\pi} \alpha_2 d\phi = n_2 h,$$

where r_1 and r_2 are the roots of the equation $S(1/r)=0$. This gives

$$\left. \begin{aligned} -2\pi \left\{ e_1 e_2 \sqrt{\frac{m_1 m_2}{-2\alpha_1(m_1 + m_2)}} \left[1 + \frac{2\alpha_1}{(m_1 + m_2)c^2} \right] \right. \\ \left. + \sqrt{\alpha_2^2 - \frac{4m_1 m_2 e_1^2 e_2^2}{(m_1 + m_2)^2 c^2}} \right\} = n_1 h, \\ 2\pi \alpha_2 = n_2 h. \end{aligned} \right\} \quad (34)$$

The constant α_1 measures the sum of kinetic and potential energy of the system, and is very small compared with $\epsilon = (m_1 + m_2)c^2$, which is the amount of energy stored in the masses. Thus the second term in the square bracket of the first equation (34) is very small compared with unity.

And so is the expression $\frac{4m_1 m_2 e_1^2 e_2^2}{\alpha_2^2 (m_1 + m_2)^2 c^2}$. If we neglect them, we find in first approximation for α_1 the value

$$-\alpha_1^0 = \frac{2m_1 m_2 \pi^2 e_1^2 e_2^2}{(m_1 + m_2) h^2 (n_1 + n_2)^2} \dots \dots \dots (35)$$

This is the value of α_1 when magnetic forces are neglected. Substituting this approximate value in the small term of (34), and neglecting the powers of $\frac{\alpha_1^0}{\epsilon}$ which are higher than the first, we find easily

$$-\alpha_1 = -\alpha_1^0 \left[1 - \frac{8\alpha_1^0}{\epsilon} \left(\frac{1}{2} + \frac{n_1}{n_2} \right) \right] \dots \dots \dots (36)$$

The corresponding formula for the relativity effect * is

$$-\alpha_1 = -\alpha_1^0 \left[1 - \frac{2\alpha_1^0}{\epsilon'} \left(\frac{1}{4} + \frac{n_1}{n_2} \right) \right], \quad . \quad . \quad . \quad (37)$$

where $\epsilon' = m_1 c^2$ is the amount of energy stored in the electron. We see that both effects are of much the same kind: the spectral lines are shifted and split into a number of components. But the relativity effect is by much the

larger, since we have approximately $\epsilon' = \frac{m_1 \epsilon}{m_2}$. Thus the

shifting effect of the magnetic action is $\frac{8m_1}{m_2}$ times that of

the relativity, and the splitting effect $\frac{4m_1}{m_2}$ times. For a

hydrogen atom the figures are 1/230 and 1/460.

For the Balmer series of hydrogen, the end trajectories correspond to $n_1 + n_2 = 2$: a circular one with $n_1 = 0, n_2 = 2$, and an elliptic one with $n_1 = n_2 = 1$. On account of the relativity effect, the lines are doublets for which the theoretical value of difference of wave-numbers is 0.365. The last decimal of this figure is already beyond the limit of accuracy of modern wave-length measurements. Accordingly the 430 times smaller effect of the magnetic forces can in no way be checked experimentally.

The effect of magnetic forces is to increase slightly the relativity effect. But from the formulæ of the first part of this paper we can easily show that the relativity effect is on the other hand slightly decreased by the fact that the nucleus is not fixed, as it is assumed to be in Sommerfeld's theory. The correction is of the same order as the one just computed. Thus both corrections partly cancel each other.

* See, for instance, J. H. Jeans, 'The Dynamical Theory of Gases,' 3rd edition, p. 424.

XI. *On the Theory of Metallic Conduction.* By TCH. BIALOBJESKI, *Professor in the University of Cracow (Poland)* *.

THE electron theory of metallic conduction, notwithstanding some serious objections raised against it, is still in favour at the present time as giving the best interpretation of facts in this field of physical inquiry. But the investigations of Kamerlingh Onnes on the electrical conductivity of some pure metals in the proximity of absolute zero (0° K.) showed that insurmountable difficulties stand here in the way. Kamerlingh Onnes discovered that at the temperature of liquid helium (about 4° K.) some metals pass into a state of super-conductivity, their specific resistance being less than one 10^{-11} part of that at 0° C. The super-conducting state appears abruptly at a definite temperature. On the free-electron theory the electrical conductivity of a metallic body is given by the formula

$$c = \frac{ne^2 l \bar{v}}{6RT} \dagger,$$

where n denotes the number of free electrons in unit volume, e is the elementary charge of electricity, l the mean free path of an electron, $\bar{v}$ the mean velocity of thermal agitation of electrons, R the gas constant calculated for one molecule, T the absolute temperature. An enormous increase of conductivity at 0° K. might be attributed to an increase of the free path; but such an almost unlimited lengthening is hardly conceivable. Other attempts aiming at reconciliation of the theory of free electrons with experimental data cannot be regarded as satisfactory.

In the year 1915 Sir J. J. Thomson restated his theory which had been considered in the book on the 'Corpuscular Theory of Matter' as the second theory of metallic conduction, the first being that of free electrons ‡.

According to this theory atoms of metals contain electrical doublets, i. e. pairs of equal and opposite charges at short distance one from the other. In the absence of external electrical force the axes of doublets are uniformly distributed, having all directions in space. When an electrical force acts on the body the axes of the doublets tend to point

* Communicated by the Author.

† See, for instance, Jeans, 'Dynamical Theory of Gases,' 2nd edition, p. 319.

‡ Phil. Mag. xxx. p. 192 (1915).

in the direction of the force and the moments of the doublets acquire a finite resultant, whose direction of course coincides with that of the force. If no disturbing influences were at work, the smallest electrical force would be sufficient to produce the maximum polarization, *i. e.* to arrange the axes of all doublets in one direction. The thermal agitation (and perhaps some other influences) put a limit to the polarization produced by a given electric force.

A characteristic feature of the new aspect of Sir J. J. Thomson's theory is the introduction of an intermolecular field of force; this makes the view of the conductivity of metals similar to that by which Weiss explained ferromagnetism. It is assumed that, when the external force is applied, a new force arises acting on the doublets and proportional to the polarization of the body. If N is the number of doublets in unit volume, M the electrical moment of a doublet, I the polarization of unit volume (that is, the resultant of all moments in the direction of electric force),

we might imagine that $\frac{I}{M}$ doublets have their axes pointing

in the direction of the force and forming atomic chains, while the axes of the other doublets are distributed uniformly in all directions. The peculiarity of metals among other substances is that some electrons are very loosely connected with the atoms. Consequently along atomic chains an interchange of electrons between atoms is going on continuously. Let us suppose that p electrons pass along each chain per second. Denoting by d the distance of the

adjacent atoms in the chain, we have $\frac{Id}{M}$ chains crossing unit area at right angles to the electric force. The current through unit area is then

$$i = ep \frac{Id}{M} \dots \dots \dots (1)$$

The relation between I and the extraneous electric force is very complicated; indeed, the disturbing effect of molecular motion and the action of intermolecular forces must be taken into account. The explanation of super-conductivity, however, presents no difficulty. The rôle of electric force in metallic conduction is mainly to form chains; at low temperatures the disturbing effect of thermal energy vanishes, so that intermolecular forces become preponderant: the chains persist after the electric force is removed and electrons are transmitted continually along them.

The form given to the theory by Sir J. J. Thomson seems to be open to objection. The recent progress of our views on the dependence of various phenomena upon temperature has led to the conviction that Planck's quanta should be introduced into all problems concerning partition of energy. As the thermal agitation plays a prominent part both in electrical and thermal conductivity, the introduction of quanta into the theory of these phenomena seems unavoidable. Therefore Thomson's theory, resting on the rule of equipartition and taking no account of striking departures from this rule at the proximity of 0° K., must be regarded as insufficient. Moreover, the assumption of intermolecular fields of force is of a somewhat vague character. It is the object of this paper to show that the hypothesis of intermolecular fields of force, considered as an important agent of conductivity at low temperatures, becomes unnecessary if we introduce energy quanta. It will be seen that combining Sir J. J. Thomson's hypothesis regarding the interchange of electrons between atoms with the fundamental relations of the quantum-theory, we are led to an interpretation of essential features shown by the conduction of electricity through metals.

Let X stand for the extraneous electric force acting on a metallic conductor. Applying the well-known formula of Boltzmann, Langevin has obtained in his theory of paramagnetism an expression for the polarization of unit volume, which may be used in our case without any change. We have

$$I = NM \left(\frac{ex + e^{-x}}{e^x - e^{-x}} - \frac{1}{x} \right),$$

where $x = \frac{MX}{RT}$ According to classical statistical theory,

$\frac{1}{2}RT$ represents the mean energy corresponding to one degree of freedom in a system, which is in thermal equilibrium with a gas at T° K. At present the opinion has prevailed that this statistical inference is only true at high temperatures and is utterly inapplicable at very low temperatures. An expression for the mean energy belonging to one degree of freedom has been given by Planck in the first form of his theory as

$$\frac{1}{2} \frac{h\nu}{e^{\frac{h\nu}{RT}} - 1},$$

h being Planck's universal constant, ν the frequency of

M 2

oscillations corresponding to the degree of freedom under examination. We assume the thermal agitation to be resolved as an assemblage of homogeneous vibrations having a definite scale of frequencies. It is known that Debye, and independently Born and Kármán, have analysed in this way the thermal vibrations of bodies with crystalline structure. It will be natural to suppose that the atoms of metals containing doublets are performing similar vibrations, by which the directive action of electric force is disturbed in accordance with Boltzmann's rule giving Langevin's formula. Consequently we retain unchanged the expression of I putting herein

$$x = MX : \frac{h\nu}{e^{RT} - 1}.$$

In order to obtain simple relations let us admit only one frequency of atomic vibrations. Although this assumption might be deemed a too great simplification, the general features of the phenomena under consideration will not be essentially modified. The electric current will now be represented by the expression :

$$i = \frac{epdI}{M} = Nepd \left(\coth x - \frac{1}{x} \right), \quad . \quad . \quad . \quad (2)$$

where $x = \frac{MX \left(e^{\frac{h\nu}{RT}} - 1 \right)}{h\nu}.$

Let us call Langevin's function and denote by $L(x)$ the expression in brackets. Expansion of $L(x)$ in an ascending series gives

$$L(x) = \frac{x}{3} - \frac{x^3}{45} + \dots$$

At high temperatures we may use approximate formulas :

$$x = \frac{XM}{RT} \quad \text{and} \quad L(x) = \frac{x}{3} = \frac{XM}{3RT}.$$

In this case

$$i = \frac{NMe pd}{3RT} \cdot X; \quad . \quad . \quad . \quad . \quad (3)$$

the conductivity at high temperatures will be expressed by

$$c = \frac{NMe pd}{3RT} \cdot . \quad . \quad . \quad . \quad (3')$$

More precise results can be obtained by using the results of Debye's calculation relating to the spectrum of thermal vibrations*. When N molecules participate in the elastic vibrations (identified with the thermal energy of the body), then the number of vibrations with frequencies contained between ν and $\nu + d\nu$ is

$$3N \frac{\nu^2 d\nu}{\nu_m^3};$$

the maximum frequency of the vibrations is here denoted by ν_m . Thus

$$i = \frac{3Nepd}{\nu_m^3} \int_0^{\nu_m} L(x) \nu^2 d\nu. \quad . \quad . \quad . \quad (4)$$

We do not endeavour to investigate this equation exactly and shall content ourselves with the examination of conductivity at higher temperatures. Writing approximately

$$e^x = 1 + x + \frac{1}{2}x^2,$$

we get

$$L(x) = \frac{1}{3}XM \left(\frac{1}{RT} + \frac{h\nu}{2R^2T^2} \right),$$

and by integration

$$i = \frac{NMepd}{3RT} \left(1 + \frac{3}{8} \frac{\theta}{T} \right) X, \quad . \quad . \quad . \quad (5)$$

introducing Debye's characteristic temperature by the equality

$$\theta = \frac{h\nu_m}{R}.$$

Thus the temperature coefficient of conductivity is greater than that of perfect gases. This conclusion is in accordance with experimental data concerning pure metals. Iron and nickel on Debye's theory of specific heat are distinguished by an exceptionally high value of the characteristic temperature ($\theta^{\text{Fe}} = 467$, $\theta^{\text{Ni}} = 435$); the same metals have particularly considerable temperature coefficients of conductivity which agrees with (5).

Using the simplest expression (3') for conductivity at comparatively high temperatures we proceed to calculate

* *Annalen d. Physik*, xxxix. p. 789 (1912).

the value of p , the number of electrons which pass per second along the atomic chain :

$$p = \frac{3RTc}{NMed}.$$

We will apply this equation to the case of silver ($c = 1.500$ E.M.U. at 0° C.). For the values of constants R , N , e we take :

$$N = \frac{6.1 \cdot 10^{23} \cdot 10.5}{108}, \quad e = 1.6 \cdot 10^{-20}, \quad R = 1.4 \cdot 10^{-16}.$$

The moment of a doublet $M = e\delta$, where δ is the distance of two oppositely charged constituents, we take to be equal to $1.6 \cdot 10^{-20} \cdot 10^{-8}$. For the distance of two neighbouring atoms we put $d = 3 \cdot 10^{-8}$ (equal to the linear constant of the crystalline lattice of calcite). The two last numbers do not pretend to give more than the true order of magnitude. We obtain thus $p = 1.7 \cdot 10^{16}$. It will be observed that this number corresponds to frequencies of electromagnetic vibrations in the region lying between the ultraviolet and the softest X radiations.

From what has been said it follows that the crucial test of the theory will be its application to the conductivity at very low temperatures. We note that at 0° K., x is equal to exponential infinity and $L(\infty) = 1$. Then

$$i_0 = N e p d, \quad \dots \quad (6)$$

which gives for silver $4.8 \cdot 10^{11}$ E.M.U. This monstrous current arises if all the atoms of a piece of metal are arranged in parallel chains and may be started by an arbitrarily small electromotive force. It should not, however, be inferred that such a current can be excited almost spontaneously and instantly. In order to accumulate the enormous energy of magnetic field a corresponding amount of work must be done. As soon as the current has arisen, the smallest electric force would be sufficient for maintaining it: we have, therefore, super-conductivity. At the same time i_0 represents maximum or saturation current.

We shall now give the formulas expressing changes of current as a function of temperature and electromotive force. From (2) we deduce :

$$\frac{di}{dx} = \frac{i_0}{x} \left(\frac{1}{x} - \frac{4x}{(e^x - e^{-x})^2} \right), \quad x = \frac{XM}{h\nu} (e^{\frac{h\nu}{RT}} - 1). \quad (7)$$

At the proximity of 0° K. , commencing, say, from 8° K. , when x acquires very great values, the differential coefficient becomes exceedingly small; we have then a saturation current, independent of electromotive force and equal to i_0 . At these temperatures the thermal agitation ceases to destroy perceptibly the directive action of electrical forces. We have also:

$$\frac{di}{dT} = i_0 \frac{XM}{RT^2} e^{\frac{h\nu}{RT}} \left(\frac{4}{(e^x - e^{-x})^2} - \frac{1}{x^2} \right). \quad (8)$$

The value of this derivative is also infinitely small near 0° K.

It seems that not all metals are able to pass into a superconducting state; some of them, at very low temperatures, tend to acquire a constant conductivity, enormous but finite. This behaviour is proper to metals containing foreign admixtures and especially to alloys. For the purpose of extending the theory to these cases, Sir J. J. Thomson introduces an additional restoring couple, which tends to make the axes of doublets to take up a definite direction, determined by the structure of the body.

This supposition may be immediately adapted to the form of theory here developed. Let us consequently admit that besides an electrical force and disturbing action of thermal energy there exists a couple D acting on the doublets. The equations (2) or (4) maintain their form, but the quantity denoted by x will be changed; we now have

$$x = XM : \left(\frac{\frac{h\nu}{RT}}{e^{\frac{h\nu}{RT}} - 1} + D \right);$$

not only the thermal agitation, but also the couple D opposes the directive action of the electric force. It is evident that the limiting value of Langevin's function in the proximity 0° K. , instead of unity will now be

$$\lim_{T=0} L(x) = \coth \left(\frac{XM}{D} \right) - \frac{XM}{D};$$

the current tends to the value

$$i_0' = N e p d L \left(\frac{XM}{D} \right). \quad (9)$$

If D is not vanishingly small, i_0' will appear considerably less than i_0 and a clearly expressed saturation will not come

into existence. At higher temperature by using (4) and putting

$$L(x) = \frac{1}{3} \frac{XM}{RT + D}$$

we get

$$i = \frac{NMepd}{3(RT + D)} X;$$

therefore in the equation

$$\sigma = \sigma_0(1 + \alpha_1 t)$$

giving the resistance σ as a function of temperature, the coefficient

$$\alpha_1 = \frac{\alpha}{1 + \frac{\alpha D}{R}},$$

where α denotes the temperature coefficient of perfect gases. We see that $\alpha_1 < \alpha$, which is in agreement with experimental results in the case of alloys possessing probably a relatively strong restoring couple D .

We add in conclusion that by accepting the above deductions one must adopt a definite attitude with respect to the problem of existence of energy in a body at 0° K. In the second modified version, which Planck gave to his theory, a degree of freedom possesses a mean energy equal to

$$\frac{1}{2} \left(\frac{h\nu}{2} + \frac{h\nu}{e^{RT} - 1} \right).$$

If we had to put this value in the Langevin's function, we should obtain at 0° K.

$$x = \frac{2XM}{h\nu},$$

which in the case of not very high electromotive force is far less than unity. The super-conductivity could not be observed and even there would not exist a rapid increase of conductivity at low temperatures. We must therefore conclude that either metals do not possess energy at all at the absolute zero of temperature or the corresponding amount of vibratory energy $\frac{h\nu}{2}$ is not heat energy.

Cracow (Poland).

June 24, 1921.

XII. *The Evaluation of the Colours of the Spectrum in Terms of the Three Primary Colours.* By Dr. R. A. HOUSTOUN, *Lecturer on Physical Optics in the University of Glasgow,* and ERIC DOW, *B.Sc.* *

IF we take three colours—a red, a green, and a blue,—and represent them by the corners of an equilateral triangle, then any colour whatever can be represented by a point in the plane of the triangle. The three colours at the corners are referred to as the primary colours. Any colour obtained by mixing the primaries is represented by a point inside the triangle, and any colour, such as violet, that cannot be obtained by mixing the primaries, is represented by a point outside the triangle. Any colour obtained by mixing two colours is represented by a point on the straight line joining these two colours which divides the distance between them inversely in the ratio of their intensities. That is, to find the position of the mixture we regard the colours as particles the masses of which are proportional to their intensities, and proceed to find the centroid of these particles.

The laws of colour-mixing as expressed in the triangle diagram are facts of experience independent of all theories of colour-vision, and they are accepted by all theorists. It is the additional assumption, that to each of the primary colours there corresponds a primary-colour sensation, that has been a matter of dispute. The colour diagram was introduced by Newton in his 'Opticks,' and was fully developed by Helmholtz and Maxwell a century and a half later.

The position of the colours of the spectrum on the triangle diagram has been determined by Maxwell †, by König and Dieterici ‡, and by Abney § (twice); and the results of these observers have obtained considerable publicity, the curves of König and Dieterici in particular having been copied into many text-books. The different observers expressed their results in different units; in 1919, Dr. Houstoun || calculated them into the same units, and found that the agreement was not good, also that in no case were all the necessary particulars of the determination recorded. It was decided, therefore, to investigate the matter afresh.

Considerable care was bestowed on the selection of the

* Communicated by the Authors.

† Phil. Trans. 150, p. 57 (1861).

‡ Berl. Ber. p. 805, 1886.

§ Phil. Trans. 193A, p. 259 (1900), and 205A, p. 333 (1906).

|| Phil. Mag. xxxviii. p. 402 (1919).

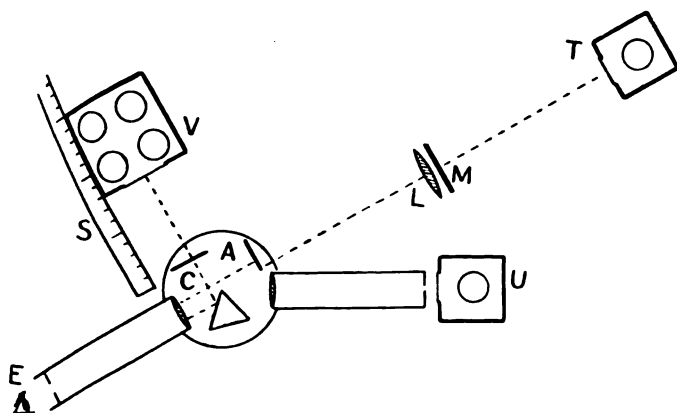
method. First of all a method based on Maxwell's colour box was tried. Thirty-two adjustable slits were set up at one side of a room in two rows of sixteen, and illuminated by tungsten-filament lamps; these were viewed through a prism and a telescope which had its eyepiece removed and a slit substituted. A biprism was mounted behind the prism. A preliminary determination by this apparatus was made by Mr. James Hyslop in the first months of 1920. The method was, however, abandoned, as it did not seem any better than Maxwell's.

The next attempt was based on König and Dieterici's method, and involved a quartz prism and nicol eyepiece, and was made in the autumn of 1920. This method was, however, little more than explored, as it seemed neither easy nor accurate. Finally, during the past winter a method was evolved which was both elegant and simple, and a great advance on the methods hitherto used. It does not make the determination easy; the actual matching of the colours will always remain a tedious business and require great care. But it removes all adventitious sources of error and worry connected with the apparatus, and leaves one with nothing but the actual difficulty of matching the colours itself. And as it does not require the intensities to be equal when the colours are matched, the matching is easier than by the other methods which involve heterochromatic photometry. Another advantage of the new method is the simple geometric procedure for evaluating the results.

Fig. 1 represents the apparatus. A is a ground-glass plate, called the comparison field. T is a 40-watt Osram lamp in a box with a square ground-glass window. Except for the window the box was light-tight, but at the same time adequate provision was made for its ventilation. The lens L focussed an image of the window on A. In front of the lens L was the colour mixer M; this consisted of a rectangular opening, across which one of three colour filters could be screwed. These filters were made of Wratten and Wainwright standard tricolour film mounted in B quality glass; the first was half red and half green, the second half green and half blue, and the third half blue and half red. If the first filter was screwed across the aperture, the film covering the latter changed from red to green, and the colour of the image on A changed simultaneously from red to green. For intermediate positions of the filter the colour of the image on A was a mixture of red and green, the amount of each component in the mixture being proportional to the

area it covered on the lens. The colour of the image on A was of course always perfectly uniform. The area of the lens covered by each colour could be read off on a scale. By means of the three filters the colour of the image on A could be changed from red through orange, yellow, and yellowish-green to green, from green through peacock-blue to blue, and from blue through purple, magenta, and carmine back to red.

Fig. 1.



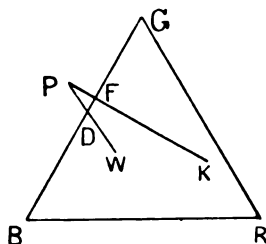
The ground-glass A stands on the table of a spectrometer, the telescope and collimator of which had been interchanged. In front of the collimator slit is a light-tight box U, with a ground-glass window containing a 40-watt Osram lamp. The prism is a 60° dense flint one, the faces of which measure 3.5 x 3.1 cm.²; it stands at minimum deviation for Na light. The eyepiece of the telescope is removed and a slit substituted; this slit is 1 millimetre wide. An eye E looking in at the telescope consequently sees the face of the prism uniformly illuminated by whichever colour of the spectrum falls upon this slit and beside it the comparison field A. As the prism has a sharp edge, the two bound one another very sharply.

C is another ground-glass plate standing on the spectrometer table. It is illuminated by four 40-watt Osrams in a light-tight box V with a ground-glass window. The luminosity of C varies roughly according to the inverse square of its distance from the window. The eye at E sees the surface C superimposed by reflexion on the face of the

prism. The position of the box V can be read on the scale S.

Let us now consider the theory of the method. In fig. 2 the points R, G, and B represent the colours of the tricolour filters when placed in front of a diffusing surface illuminated by an Osram lamp. Consequently, when the colour mixer is fitted in succession with the red-green, the green-blue, and the blue-red filter, the comparison field can be given all the colours represented by the three sides RG, GB, and BR respectively. In the ordinary use of the apparatus, therefore, the comparison field is restricted to the sides of the triangle.

Fig. 2.



Suppose now that we wish to find the position on the diagram of a colour in the blue-green part of the spectrum. We know that the spectrum colours owing to their purity lie outside the triangle; the colour in question will lie at some such point as P. The collimator is turned until the face of the prism is illuminated with the colour in question. The lamps V (fig. 1) are then turned on; let us suppose that their light is represented by some such point as W. The face of the prism being illuminated by a mixture of white light and the spectrum colour is represented by a point on the line PW. The distances of the lamps V and the colour mixer are adjusted until the colours of the prism face and the comparison field are exactly the same. They must then both be represented by the point D. Now the ratio GD/DB is obtained from the reading of the colour mixer. Consequently the point D is fixed, and P is restricted to the line WD.

Let a piece of coloured gelatine be placed in front of C' (fig. 1), so that the light obtained by reflexion from the prism has some such position as K (fig. 2). Then, as the box V is moved along the scale, the colour of the prism face

travels along the line KP. If the colour mixer and the distance of the box V are adjusted so that the face of the prism and the comparison field have exactly the same colour, this colour must be represented by the point F. The ratio GF/FB is then obtained from the reading of the colour mixer: consequently F is fixed, and P is restricted to the line KF. As it is now restricted to two intersecting straight lines, its position is completely determined. The positions of the other spectrum colours can be obtained in the same way. Instead of using the line KP we might have taken the line RP.

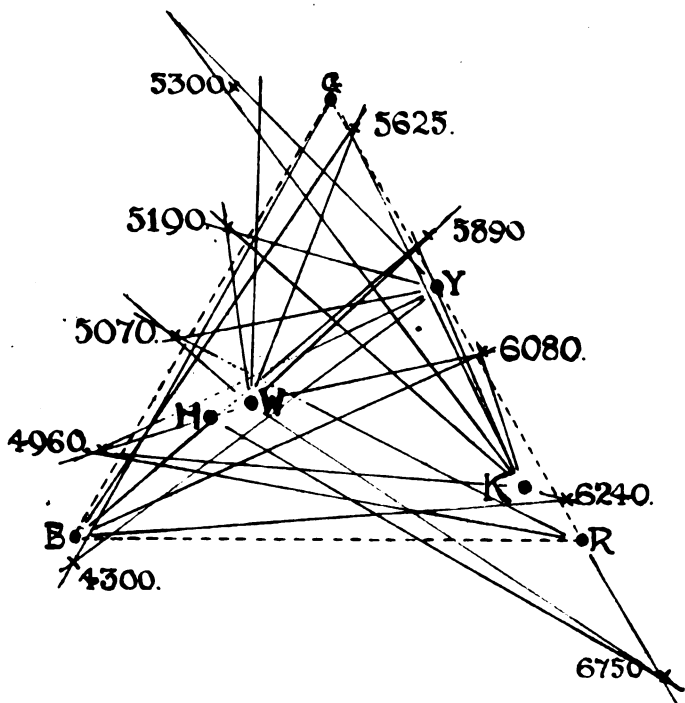
It remains to explain how the positions of W and K in fig. 2 were determined. Four such points were used altogether: W, which was obtained by letting the light from V fall directly on C, as already mentioned; Y, which was obtained by placing a yellow filter (the Wratten minus-blue) immediately in front of C; K, which was obtained by placing a pale red filter in front of C; and H, which was obtained by substituting one 100-watt half-watt lamp for the four Osrams and not using any filter. Their positions on the diagram were obtained by turning out the lamp U (fig. 1), so that the prism face was illuminated solely by reflected light and manœuvring special filters each containing red, green, and blue film over the lens until a match was obtained. Then the areas of each colour covering the aperture were noted; they specified the position of the point.

In matching the colours of the prism face and the comparison field, it is not necessary that their intensities should be exactly the same. It is, however, advisable that there should not be much difference between them. In addition to altering the distance of V and changing the width of the collimator slit, the intensities were also regulated by placing additional pieces of ground-glass in front of the windows in T and U, and by fixing wire gauze of different size of mesh immediately in front of M.

There were various screens for cutting off stray light which are not shown in fig. 1. There was a switch-board close to the observer's left hand for controlling the lamps T, U, V, and a reading-lamp, and beside the switch-board a cord for moving V, while with his right hand he could reach the screw motion for the colour mixer and the screw motion for the collimator. The spectrometer read to one minute of arc, and the lenses of telescope and collimator were of 1 inch diameter.

A series of results obtained by Mr. Dow is shown in fig. 3. These were verified by Dr. Houstoun, and found to agree fairly well with the values he obtained. It will be observed that generally more than two, in one case as many as four, lines were obtained to determine the point. The closeness of intersection of the different lines gives an idea of the accuracy of the method. From the directions of the lines it is possible to ascertain which auxiliary colours were used on the ground-glass plate C.

Fig. 3.



Each point took as a rule one day, as the eye required a long rest before each setting. Also the positions of the points were not the same on successive days. This was noted particularly by Dr. Houstoun in the case of the point in the extreme red, 6750 A.U., when testing whether the intensity of the light made an appreciable difference in the position of the point: of two determinations

made on different days of the same week one agreed closely with the position given on the diagram, and the other was almost twice as far out from the corner of the triangle. As the observations were made with the greatest of care and under exactly the same conditions on each occasion, and similar differences had been noticed on former occasions, there seems no doubt that the colour-vision changes appreciably from day to day.

The luminosity of the comparison fields was about 100 metre-candles when working in the red end and middle of the spectrum, but it fell off to about 5 metre-candles towards the violet end. When the luminosity was diminished to one-quarter, it was found that there was no appreciable change in the positions of the points. In the diagram, red, green, and blue are measured in units of different luminosity, the relative values of the units for the normal eye being about 100, 120, and 5 respectively. Thus the point represented by the centroid of the triangle contains about 20 times as much red as blue and 24 times as much green as blue, although it would be produced by placing equal areas of the three filters in front of a lens forming an image of a piece of ground-glass illuminated by an Osram lamp. To produce the colour containing equal quantities of the three lights, we would require to place a much larger area of blue filter in front of the lens. This colour would be represented by a point near the blue corner of the triangle. On account of this difference in the size of the units, the colour changes most rapidly in the neighbourhood of the blue corner.

As represented on the diagram, the colour of the Osram lamp is 19.6 red, 30.1 green, and 50.3 blue, and the colour of the half-watt lamp 13.3 red, 27.1 green, and 59.8 blue. Daylight from a north sky, as determined by an auxiliary experiment, was at 8 red, 20 green, and 72 blue on the diagram.

It will be observed from the diagram that the wave-lengths 6750, 6240, 6080, 5890, and 5625 are in a straight line. Then the curve bends, and the remaining points are approximately on another straight line. This is in agreement with the determinations made by previous investigators which were reduced to the same units by Dr. Houstoun in the paper already cited, only previous investigators all make the bend nearer the violet end of the spectrum, and have the curve straight from the red end almost to 5128. That is, all the points from 6750 to 5190 should be on a straight line, which is in flat contradiction to the results we have obtained.

While there is no doubt that the curve continues straight for a good part beyond 5625 and while 5300 is a point difficult to fix, there is no doubt whatever about the position of 5190.

The corners of the triangle make very good matches with 6500, 5550, and 4800 respectively.

There is no doubt whatever that the extreme violet point 4300 contains some red, and lies on the red side of the line BG. It is quite impossible to reproduce B by mixing G and 4300. The difference seems trifling on the diagram, but that is only because owing to the small luminosity of the blue unit the colours change very rapidly in the neighbourhood of B. The results that the red end of the curve is straight, while the violet end curves back towards red, are in agreement with a special investigation on these points which was carried out by Lord Rayleigh*.

It was stated in the paper already cited that the different attempts hitherto made to resolve the colours of the spectrum into primary colours are not in good agreement. As a result of our investigation, we are of opinion that this is because the subject does not admit of very exact measurement; besides the differences which occur between different observers, the measurements made by the same observer vary somewhat from time to time. The descriptions of the previous investigations give an impression of fictitious accuracy. Newton† himself stated that the diagram was accurate enough for practice, though not mathematically accurate.

Summary

(i.) A new method of great simplicity and elegance has been worked out for evaluating the spectral colours in terms of the primary colours.

(ii.) A set of values has been obtained by this method.

(iii.) In descriptions of previous work on the subject sufficient attention has not been called to the variation in the performance of the same eye from day to day.

September 1, 1922.

* Scientific Papers, vol. v, p. 569.

† 'Opticks,' Bk. i. Pt. 2, Prop. VI. Prob. II.

XIII. *The Equality of Tensors.* By T. Y. THOMAS *.

THE components of a tensor represent physical quantities, or else are such that physical quantities can be expressed in terms of them, as by differentiation for example. By equating the components of two tensors, relations between these quantities, *i. e.* physical laws, are obtained in a form which remains the same in all coordinate systems. The conditions under which the components of one tensor are equal to the components of another are therefore of fundamental importance. So far, these conditions have been furnished by Theorem I. of this paper. Theorem II., however, gives an entirely new set of conditions and promises to have important applications. It was suggested by a passage in Einstein's Princeton Lectures on the momentum and energy of moving bodies, and is applied to this problem in the present paper.

Definition of tensor.—A tensor of the n th order is a set of k^n functions of k variables which is transformed according to one of the following schemes :

$$\bar{A}^{ab\dots c} = \frac{\partial y_a}{\partial x_\alpha} \frac{\partial y_b}{\partial x_\beta} \dots \frac{\partial y_c}{\partial x_\gamma} A^{a\beta\dots\gamma},$$

$$\bar{A}_{ab\dots c} = \frac{\partial x_a}{\partial y_\alpha} \frac{\partial x_b}{\partial y_\beta} \dots \frac{\partial x_c}{\partial y_\gamma} A_{a\beta\dots\gamma},$$

$$\bar{A}^{a\dots b}{}_{c\dots d} = \frac{\partial y_a}{\partial x_\alpha} \dots \frac{\partial y_b}{\partial x_\beta} \frac{\partial x_\gamma}{\partial y_c} \dots \frac{\partial x_\delta}{\partial y_d} A^{a\dots\beta}{}_{\gamma\dots\delta},$$

where the indices which appear twice are to be summed over the values $(1, 2, \dots k)$. Each A carries n indices. The tensor is contra-variant, co-variant, or mixed respectively according as its scheme of transformation is the first, second, or third of these equations. The functions A are the components of the tensor in the coordinate system considered.

Definition of equality.—Two tensors of the same kind (contra-variant, co-variant, or mixed) and of the same order will be said to be equal if their corresponding components are equal in all coordinate systems.

THEOREM I. If the components of a tensor A are equal to the corresponding components of a tensor B , of the same kind and order as A , in one coordinate system, then A and B are equal.

* Communicated by Prof. Oswald Veblen.

Proof.—Taking A and B to be mixed tensors as the most general case, we have

$$\begin{aligned} & (\bar{A}^{a\dots b}_{c\dots d} - \bar{B}^{a\dots b}_{c\dots d}) \\ &= \frac{\partial y_a}{\partial x_a} \dots \frac{\partial y_b}{\partial x_b} \frac{\partial x_\gamma}{\partial y_c} \dots \frac{\partial x_\delta}{\partial y_d} (A^{a\dots b}_{\gamma\dots\delta} - B^{a\dots b}_{\gamma\dots\delta}) = 0, \end{aligned}$$

since from the conditions of the theorem,

$$A^{a\dots b}_{\gamma\dots\delta} = B^{a\dots b}_{\gamma\dots\delta}.$$

Corollary.—If the components of a tensor vanish in one coordinate system, they vanish in every coordinate system.

Definition of the class of a component.—The components $A^{a_1\dots a_m}_{a_{m+1}\dots a_n}$ and $A^{b_1\dots b_m}_{b_{m+1}\dots b_n}$ of the tensor A will be said to be in the same class if when $a_i = a_j$, $b_i = b_j$, and when $a_i \neq a_j$, $b_i \neq b_j$.

The general tensor of the n th order contains $2^n - n$ classes.

In the following we shall consider only those terms for which the number of distinct indices is not greater than k , where k is the order of the space. This restriction does not exclude any tensors of practical importance, for the components of a tensor are the coefficients of the invariant $A^{a\dots b}_{c\dots d} \xi_a \dots \xi_b \xi^c \dots \xi^d$, and the terms which involve more than k distinct indices are necessarily zero.

THEOREM II. If one component α of a tensor A is equal to the corresponding component β of the tensor B, of the same kind and order as A, in all coordinate systems, then the corresponding components of the class of α and β are equal.

Proof.—From the conditions of the theorem we have

$$\bar{A}^{a\dots b}_{c\dots d} = \bar{B}^{a\dots b}_{c\dots d},$$

where $a\dots b, c\dots d = 1, 2\dots k$ have particular values. The barred components in the coordinate system y are obtained from the unbarred in the coordinate system x by an arbitrary transformation. The unbarred components are referred to an arbitrary coordinate system, so that any relation between them will hold in all coordinate systems.

Let $\bar{\alpha}\dots\bar{\beta}, \bar{\gamma}\dots\bar{\delta}$ denote particular values of $\alpha\dots\beta, \gamma\dots\delta$ such that $A^{\bar{\alpha}\dots\bar{\beta}}_{\bar{\gamma}\dots\bar{\delta}}$ is in the same class as $A^{a\dots b}_{c\dots d}$. Then we shall have

$$A^{\bar{\alpha}\dots\bar{\beta}}_{\bar{\gamma}\dots\bar{\delta}} = B^{\bar{\alpha}\dots\bar{\beta}}_{\bar{\gamma}\dots\bar{\delta}},$$

provided that we can make a transformation such that the coefficient of

$$(A^{\bar{\alpha} \dots \bar{\beta}}_{\bar{\gamma} \dots \bar{\delta}} - B^{\bar{\alpha} \dots \bar{\beta}}_{\bar{\gamma} \dots \bar{\delta}})$$

is not equal to zero, while all the other coefficients are equal to zero. A transformation of this sort is

$$\begin{aligned} y_a &= x_{\bar{a}} \\ &\dots\dots\dots \\ y_b &= x_{\bar{b}} \\ y_c &= x_{\bar{c}} \\ &\dots\dots\dots \\ y_d &= x_{\bar{d}} \\ y_e &= y_e(x_1 \dots x_k) \quad e \neq a \dots b, c \dots d. \end{aligned}$$

Corollary.—If one component of each class of a tensor A is equal to the corresponding component of a tensor B, of the same kind and order as A, in all coordinate systems, then A and B are equal.

Corollary 2.—If one component of a vector (tensor of the first order) is equal to the corresponding component of another vector of the same kind (contra-variant or co-variant), in all coordinate systems, then the two vectors are equal.

This follows from the fact that the components of a vector are all in the same class.

Application.—For the purpose of illustrating the above theorems, I shall include an application to the mechanics of the special theory of relativity.

Let m_0 denote the stationary mass of a particle, and x_1, x_2, x_3 its three space coordinates. Let x_4 denote the ordinary time t , and s the proper time, where we have

$$ds = dt \sqrt{1 - v^2},$$

v being the velocity of the particle referred to the velocity of light as unity. The quantities $m_0 \frac{dx_\nu}{ds}$ ($\nu = 1, 2, 3, 4$) have a tensor character; written in full, they are

$$\frac{m_0 x_1}{\sqrt{1 - v^2}}, \quad \frac{m_0 x_2}{\sqrt{1 - v^2}}, \quad \frac{m_0 x_3}{\sqrt{1 - v^2}}, \quad \frac{m_0}{\sqrt{1 - v^2}}.$$

It can be shown that the quantities I_1, I_2, I_3, E , formed from the three components of the momentum I (space components) and the energy E (time component), also possess

a tensor character *. Let us therefore make the assumption that

$$E = \frac{m_0}{\sqrt{1-v^2}}.$$

This is justified by the fact that the expansion gives $E = m_0 + \frac{1}{2}m_0v^2 + \frac{3}{8}m_0v^4 + \dots$, in which m_0 is equal to the stationary energy E_0 , and $\frac{1}{2}m_0v^2$ is the ordinary expression for the kinetic energy. To these are added terms of the fourth and higher powers of v , which are very small in comparison with $\frac{1}{2}m_0v^2$ for bodies moving with ordinary velocities. We therefore have two tensors of the first order with their fourth components equal in all coordinate systems, and hence from Theorem II. (corollary 2)

$$I_1 = \frac{m_0 v_1}{\sqrt{1-v^2}}$$

.....

$$I_3 = \frac{m_0 v_3}{\sqrt{1-v^2}}.$$

Since the force Q acting on the particle is equal to the rate of change of the momentum I , we obtain the vector equation

$$Q = \frac{dI}{dt},$$

or

$$Q_\nu = \frac{d}{dt} \left(\frac{m_0 v_\nu}{\sqrt{1-v^2}} \right) \quad \nu = 1, 2, 3.$$

Let Q_4 = the work done on the particle in unit time, then

$$Q_4 = \frac{d}{dt} \left(\frac{m_0}{\sqrt{1-v^2}} \right).$$

These are the equations of motion of the mass point.

The equations of motion for the case of a continuous distribution of matter may be obtained as follows. Let P_1, P_2, P_3 denote the three components of force on unit volume, and P_4 the work performed on unit volume in unit time. It can then be shown that P_ν ($\nu = 1, 2, 3, 4$) has a tensor character †. We have

$$P_\nu dV = Q_\nu$$

and

$$dV = dV_0 \sqrt{1-v^2},$$

* Einstein Princeton Lectures.

† Weyl, *Raum-Zeit-Materie*, 4th ed. p. 150.

dV and dV_0 referring respectively to the moving and stationary volume element. From these and the four equations above for the motion of the mass point, we can obtain

$$P_\nu = \rho_0 \frac{du_\nu}{ds} \quad \nu = 1, 2, 3, 4,$$

where

$$u_\nu = \frac{dx_\nu}{ds},$$

and ρ_0 is the stationary density of the matter. Since P_ν and $\rho_0 \frac{du_\nu}{ds}$ have a tensor character, these equations retain their form under all transformations by Theorem I.

My thanks are due to Professor Veblen, Dr. McDuffee, and Dr. Franklin for criticism and suggestions.

Princeton University,
May 1922.

XIV. *Relative Visibility of Spectra when an Electric Discharge is passed through the Vapours of Alkali Amalgams.* By F. H. NEWMAN, D.Sc., F.Inst.P., Head of the Physics Department, University College, Exeter*.

[Plate I.]

1. INTRODUCTION.

WHEN an electric discharge is passed through a mixture of gases or vapours, the relative visibility of the spectra of the components varies according to the conditions of the experiment. The early work of Ramsay and Collie † indicated that in a mixture of helium and hydrogen, the less helium there was present in the mixture, the lower was the pressure necessary to make its spectrum visible. The partial pressures of the components seemed to be important, and decided which of the two spectra was the brighter at a particular pressure of the whole. It is now known from Bohr's theory of the atom, that the ionization potentials of the components must be taken into account.

* Communicated by the Author.

† Proc. Roy. Soc. lix. (1896).

Atoms are capable of losing electrons when they collide with electrons possessing a definite ionizing potential, characteristic of the atom. When the electron returns to its normal position in the atom, the energy appears, in nearly all cases, as the principal series of the spectrum. Considering Bohr's assumption that radiation occurs when an electron falls from an outer to an inner orbit, combined with the assumption that complete ionization is produced much less frequently than partial ionization, *i. e.* the displacement of an electron from an orbit to one further out, it follows that radiation may occur before ionization. This resonance potential is determined by the frequency of a prominent line in the spectrum, the first line in a principal or combination series. Ionization may be brought about in ways other than by a single impact of an electron against an atom. It may arise from electron impacts against atoms in such rapid succession that the energies of the impacts are additive in effect. It may be due to a secondary effect involving combined action of radiant energy received from the surrounding atoms plus energy received by direct impact of electrons. At high pressures it is obvious that no appreciable ionization can occur as a result of single impacts, since the electrons, whenever emitted, would collide so frequently when gaining the necessary energy for ionization, that they would certainly collide inelastically and produce radiation before acquiring the energy necessary for ionization. Thus, practically all ionization observed at higher pressures, whatever be the applied potential difference, must be due to this secondary effect.

As a rule, the higher the ionization potential of an element, the greater is the difficulty with which it can be excited to emit its line spectrum. It is well known that it is difficult to excite helium; the smallest trace of foreign gas tending to quench the helium lines. This is due to the fact that helium has the highest ionization and radiation potential of all elements, so that when it is subjected to a stimulus, this passes through the more easily excited impurities. Under most physical conditions a very small concentration of radiant atoms suffices for the production of the principal series, especially the fundamental line.

On the basis of Bohr's theory, one would expect one line after another to appear in the spectrum series as the potential is increased from the resonance potential to that of ionization. This has actually been found with mercury by Franck*, but with other vapours this is not the case.

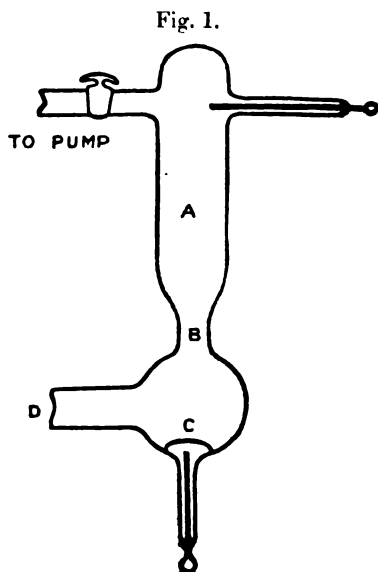
* *Zeitschrift für Physik*, xi. (1920).

It would thus appear from the laws of energy exchange between electrons and vapour molecules that in the case of a mixture of vapours of small electron affinity, the vapour having the smaller ionization potential must always emit its spectrum to a greater degree than the other vapours.

The object of the present work was to test this theory in the cases of mixtures of the vapours of mercury and the alkali metals.

2. APPARATUS.

The form of the electric discharge tube used is shown in fig. 1. It was of silica and had a constriction at B. The



mercury and the alkali were introduced, and the tube heated so that the mercury boiled. The gases liberated during the melting of the alkali were then removed by the pump. The amalgam was made the cathode, and the spectra could be viewed and photographed through the quartz window at D. In this way the light emitted at the cathode was observed. Observations also were made of the radiation emitted at B and A. The tube was enclosed in an electric heater. In obtaining the electric discharge a 10-inch induction-coil was used. It was operated with a Wehnelt interrupter joined to the 110 volt mains. Except where otherwise stated, the

amount of alkali used was always sufficient to fill the tube with its vapour at all temperatures employed. The spectrograms were photographed, by means of a constant deviation type of spectrometer, on Wratten Panchromatic plates. Some of the results obtained are shown in Plate I. The exposures were of 60 seconds' duration except (B), where the exposure was one second only. All the spectrograms were photographed at the constriction B.

3. MERCURY AND SODIUM.

With a mixture of sodium and mercury, the spectrum of the former was prominent at all temperatures. Below 100°C . the mercury spectrum was the brighter, but above this temperature the sodium D lines were more intense than the mercury lines, until at 200°C . the latter were almost entirely masked. A very brilliant yellow radiation was emitted at this temperature, and this method of obtaining the sodium D lines of great intensity is very convenient. It gave equally good results when the amalgam was heated with a gas-ring burner. If sodium alone is used in an electric discharge-tube, the vapour condenses on the colder parts of the tube and cuts off the radiation. No such trouble was experienced in the present work, and there was no blackening of the silica due to the action of the sodium vapour. The proximity of the mercury yellow lines 5769.6 and 5790.7 is not detrimental to the use of such an arrangement as a source of D-line radiation, as they are extremely faint, being almost entirely suppressed. The radiation is much brighter than that obtained with the form of sodium-vapour lamp previously described by the author*. The proportions of sodium and mercury used were about 1 and 100 respectively. The sodium radiation filled the discharge-tube, but was brightest at the constriction.

The amalgam was then removed and the tube thoroughly cleaned. Mercury alone was now placed in it, and on passing the discharge, at a temperature of 200°C ., the constriction B was filled with the D-line radiation, the sodium, having diffused into the walls of the vessel during the previous experiment, was now re-liberated by the heat. Above and below the constriction B the radiation consisted almost entirely of the mercury lines. The amount of sodium vapour necessary for the predominance of the D-lines is very

* Proc. Phys. Soc. xxxiii. pt. 2 (1921).

minute. The experiment also shows that the current density is an important factor in determining the relative visibility of the spectra of the components of vapour mixtures.

Sodium vapour has a lower ionization potential than mercury, the values being 5.13 volts and 10.2 volts respectively. It is significant, however, that Foote and Hohler* have found that the D-lines can be emitted with a potential less than 3.3 volts, while Wood and Okano† noted that the D-lines appeared when a potential of 0.5 volt only was applied.

At low temperatures, although the vapour-pressure of mercury is large compared with that of sodium, the actual values in both cases are small. As a result, the sodium atoms in the discharge-tube will be comparatively few. The mercury atoms also will probably be so far apart that the electrons attain the energy necessary to ionize the mercury atoms before they collide inelastically with any of the atoms. At low vapour-pressures therefore, it is probable that the same proportion of mercury and sodium atoms present in tube will be ionized. The intensity of the radiation emitted must be intimately connected with the concentration of the radiating atoms in the source, so that as the concentration of the radiating mercury atoms is greater than that of sodium, we should expect the mercury lines to predominate as shown in Plate I. (A).

When the temperature is increased, the vapour-pressure of mercury rises rapidly, and the electrons will now collide inelastically with the sodium and mercury atoms before they have attained energy equal to 10.2 volts—the ionization-potential of mercury vapour,—although they may attain energy sufficient to ionize the sodium atoms. In this way the proportion of the latter which are ionized may be large, while the fraction of the mercury atoms ionized decreases; so that although the mercury atoms present in the tube are far more numerous than the sodium atoms, the actual number of the former ionized may be considerably smaller than the number of ionized sodium atoms. The concentration of the latter is increased, and accordingly the D-lines predominate as shown in Plate I. (B). At higher temperatures very few of the mercury atoms are ionized owing to the high pressure, and the mercury lines become suppressed.

* Washington Acad. Sci. J. viii. (1918).

† Phil. Mag. xxxiv. (1917).

4. POTASSIUM AND MERCURY.

At temperatures below 100°C . no trace of the potassium lines was observed, Pl. I. (C). The mercury lines were prominent except 4078, which in the case of sodium and mercury had appeared to be nearly as intense as 4047. As the temperature was increased to 200°C . the potassium lines appeared, while the intensity of the mercury lines decreased, Pl. I. (D). The former were very faint, however, and at no temperature were they as bright as the latter. The most prominent of the potassium lines were 6939, 6911, and 4863. For the sake of comparison, the spectrum obtained by passing an electric discharge through potassium vapour only at 200°C . is shown in Pl. I. (E).

The theory that a vapour having a low ionization potential should always emit its spectrum to a greater extent than one having a high ionization potential, apparently fails in this case, for the ionization potential of potassium vapour is 4.32 volts—lower than that of sodium. Even if the intrinsic brightness of the sodium D-lines accounts for the brilliance of the sodium radiation, it would be expected that the potassium line 4047 would be fairly prominent, but such is not the case. It has been shown by the author in the paper already quoted that in the case of a mixture of sodium and potassium vapours, the spectrum of the latter is easily suppressed.

The reason for the faintness of the potassium lines is not clear, but it is significant that Hebb * found that the mercury spectrum could be produced at a potential as low as 0.5 volt in an atmosphere of mercury and potassium. There is a decrease in the brightness of the mercury spectrum when the temperature increases, as there should be according to the theory developed in the case of sodium and mercury.

The smallest trace of mercury vapour in the tube results in the appearance of the mercury lines: and they are much brighter than those of potassium.

5. LITHIUM AND MERCURY.

Below 100°C . the lithium lines do not appear, Pl. I. (F), but at 200°C . they are very prominent, although never showing much tendency to mask the mercury lines, Pl. I. (G). The lithium lines are most intense at the cathode, and the constriction of the tube. The most prominent line is 6708, although 4602 is strong. The mercury line 4078 is suppressed.

* Phys. Rev. xii. (1918).

The ionization potential of lithium vapour calculated from the quantum theory is 5.38 volts, higher than that of sodium vapour. The vapour-pressure of lithium, at the temperatures used, is very low. These two facts account for the lithium lines not being as intense as might be expected at 200° C.

6. RUBIDIUM AND MERCURY.

At temperatures below 100° C. the mercury spectrum predominates, although the rubidium doublet 4201, 4214—the second doublet of the principal series—is always present, Pl. I. (H). As the temperature is raised to 200° C. the colour of the radiation in the tube changes from the characteristic green of mercury to the lilac of rubidium. At this temperature the spectrum of the latter is very bright, the mercury lines being almost suppressed, Pl. I. (J). Above 200° C. the rubidium lines were still very intense compared with the mercury lines. Only in the cases of sodium, rubidium, and caesium is the mercury green radiation masked by the radiations from these metals. Potassium and lithium do not show this effect.

The ionization potential of rubidium vapour is low—4.1 volts*—and its vapour-pressure is greater than that of sodium, lithium, and potassium. These two facts account for the greater intensity of the rubidium lines compared with those of lithium and potassium. The flame lines 6299, 6207 are present.

In this case there was considerable blackening of the quartz tube due to the action of rubidium vapour.

The suppression of the mercury spectrum, and increased brightness of the rubidium lines as the temperature increases, can be explained by a theory similar to that advanced in the case of sodium.

7. CAESIUM AND MERCURY.

Below 150° C., the mercury lines are the most intense in the spectra of a mixture of mercury and caesium vapours, although the caesium doublet 4593, 4555 is always prominent, Pl. I. (K). The radiation in the tube shows the characteristic green colour of mercury, but above this temperature the colour changes to purple, and at 200° C. it is pink. The latter is characteristic of caesium radiation. At this temperature, the mercury lines are less intense than the caesium lines, Pl. I. (L). This is very marked at the constriction of the tube. Caesium lines, other than the doublet

* Franck & Hertz, *Verh. d. Deutsch. Ges.* xx. (1919).

in the blue, make their appearance—6724, 6213,—but they are comparatively faint. The mercury line 4078 is again suppressed, Pl. I. (K).

The vapour-pressure of caesium at any particular temperature is greater than that of the other alkali metals at the same temperature. Its ionization potential (3.9 volts) is also low. It is to be expected, therefore, from what has been said previously, that the caesium lines will increase in brightness compared with the mercury lines, as the temperature is increased.

There was considerable “browning” of the quartz-tube due to the action of the caesium vapour on the silica.

8. DISCUSSION OF RESULTS.

The experimental results obtained indicate that two factors, in general, determine the relative visibility of the spectra of the components when an electric discharge is passed through a mixture of gases or vapours: (*a*) the ionization potential of the vapour, (*b*) the partial pressure of the vapour. The intensity of radiation depends on the radiant energy emitted in unit time. The amount of energy emitted during each process in which emission occurs can be calculated from the quantum relation $E = h\nu$, and this amount will be one determining factor of the intensity of the spectrum lines. Another factor will be the frequency with which the process occurs. At very low pressures in the discharge-tube the electrons collide so seldom when gaining the energy necessary to produce ionization on impact with the atom, that they do not collide inelastically before acquiring the energy necessary for ionization, providing the latter is not very large. Taking the example of sodium and mercury vapours already discussed, although there is greater probability of the sodium atoms being ionized because of their small ionization potential, at very low pressures, the electrons probably acquire energy of 10.2 volts before collision, and as a result, the chance that the requisite energy will be available for the emission of the sodium spectrum will be practically equal to the chance that it will be available for the mercury. In such circumstances we should expect that the concentration of the radiating atoms would be greater for that vapour having the greater partial pressure, *i.e.* the one having the greater number of atoms per unit volume.

When the pressure becomes greater, there is less probability of the electrons attaining large energy before collision. The maximum energy attained may be sufficient to ionize atoms of small ionization potential, such as those of sodium, but not sufficient to ionize the mercury. Although the atoms of

higher ionization potential may be more numerous, the fraction of them which radiate energy may be very small. On the other hand, there may be comparatively few atoms of the element of lower ionization potential present, but a large percentage of them will be radiating atoms. In this case we should expect the spectrum of the element of lower ionization potential to be the more prominent. The experiments described above have shown this to be true.

This theory will hold if the ionization takes place owing to single impacts by the electrons, or if the energy necessary for ionization is accumulated from successive impacts and the effect of radiation from adjacent atoms.

9. SUMMARY.

1. The relative intensity of the spectra produced when an electric discharge is passed through a mixture of the vapours of mercury and the alkali metals has been investigated.

2. At 100°C ., the mercury lines predominate, but at 200°C . the spectra of the alkali metals are brighter than the mercury spectrum. The sodium D-lines mask the mercury lines at the higher temperature. The potassium spectrum is very faint under all conditions.

3. An explanation of the effect is based on the low vapour-pressures of the alkali metals at these temperatures, and on the low values of the ionization potentials which the vapours of sodium, potassium, lithium, rubidium, and caesium have.

4. The employment of the amalgams of the alkali metals, instead of the latter, forms a useful and convenient method for obtaining the spectra of the alkali metals. A brilliant D-line radiation is obtained with sodium amalgam.

XV. *On the Theory of the Specific Heat of Liquids.*

By KÔTARÔ HONDA.*

1. **T**HE theory of the specific heat of gaseous and solid phases is already well known. The results deduced from the kinetic theory of gases agree satisfactorily with the observed facts, provided the temperature is not extremely low. The theory of the specific heat of solids first developed by A. Einstein†, and afterwards improved by Nernst‡, Debye§, and others, accords with the observed facts quite satisfactorily, provided the temperature is not very high. In

* Communicated by the Author.

† Einstein, *Ann. der Phys.* xxii. p. 180 (1907).

‡ Nernst & Lindemann, *Zeitschr. für Elektrochemie*, 1911, p. 817; *Berl. Ber.* 1910, p. 26.

§ Debye, *Ann. der Phys.* xxxix. p. 789 (1912).

this case the atomic heats of many metals are a little greater than the theoretical value 5.96. As regards the liquid phase, we have as yet no satisfactory theory; the following is an attempt to fill the above gap.

Before entering upon the theory of the specific heat of the liquid phase, it is necessary to explain the mechanism of the melting of solid substances. For the sake of simplicity we take the case of the monatomic substance, which has the same atomic form both in the liquid and solid phases. Since the solid is always a crystal or crystalline, the atoms are distributed in the space-lattice belonging to its crystal system. According to the modern view, the atom has a very complicated structure, so that it sends out its lines of force chiefly in certain definite directions, and hence the regular spacing of atoms in a solid is only possible for their definite orientations—that is, in the solid substances, free rotation of the atoms is not possible. This view is confirmed by the determination of the specific heat of solid substances. Thus each atom of a solid vibrates about its mean position with three degrees of freedom.

We may also with good reason suppose that with the above mode of rectilinear vibration the atoms are associated with small dependent rotational vibrations about their centres of mass, probably with a common period of vibrations. At the ordinary temperature this mode of rotational vibration is very small; but as the temperature rises, it increases at a steady rate. The fact that at very high temperatures the specific heat experimentally found is somewhat greater than the theoretical value 5.96 indicates the presence of this rotational vibration. On approaching the melting-point of the substance, the amplitude of this vibration attains such a value that the rotational vibration at last becomes a continuous rotation. As soon as the rotational vibration is changed into a continuous rotation, the regular spacing of the atoms breaking down, disorder begins to ensue, and therefore the rotation becomes independent of the translation. The atoms thus set free have now two or three degrees of freedom for rotation; the angular velocity of each component rotation increases to such an extent that its energy becomes equal to that corresponding to one degree of freedom of rotation. If all the atoms undergo the above change, the fusion is said to be completed, and the crystal changes into a liquid. The above is more satisfactory from a physical point of view than the view proposed by Lindemann* regarding the melting.

If the above view of fusion be correct, the heat of fusion

* Lindemann, *Phys. Zeitschr.* xi. p. 609 (1910).

consists mainly of the energy of rotation of the atoms gained during the process of fusion, the potential energy of atoms due to the small expansion of the volume during fusion being comparatively small.

Since in solids the motion of each atom is vibration, but not translation as in the case of gases, its total energy is just twice the mean kinetic energy during a complete period of vibration. Hence, according to the quantum theory, the energy belonging to each degree of freedom is given by

$$\epsilon_T = \frac{h\nu}{e^{h\nu/T} - 1},$$

where T is the absolute temperature, r the gas constant referred to one atom, h the universal constant, and ν the frequency of vibration. During the process of fusion each atom gains an energy of rotation corresponding to two or three degrees of freedom, the energy for each freedom of rotation being $\frac{1}{2}\epsilon_{T_m}$, where T_m is the melting-point. If one gram atom contains N atoms, the total energy of rotation gained by the atom is

$$N\epsilon_{T_m} (=E_{T_m}) \quad \text{or} \quad \frac{3}{2}N\epsilon_{T_m} (= \frac{3}{2}E_{T_m}),$$

according as the freedom of the liquid atom is 2 or 3. Since the atomic distances in the solid and liquid phases do not differ much from each other, the rectilinear motion of the liquid atoms is also vibratory, its amplitude remaining unchanged. Hence the translational energy of each liquid atom for one degree of freedom will also be equal to E_{T_m} —that is, the same as that of the solid state or very nearly so. In general, the change of volume during melting is very small, so that the energy required for doing the internal and external work is also small; we denote it by Q . If λ be the latent heat of fusion of a substance and w its atomic weight, we have

$$w\lambda = \frac{1}{2}nE_{T_m} + Q,$$

where $n=2$ or 3 . If we neglect Q in this relation, we have simply

$$w\lambda = \frac{1}{2}nE_{T_m} \quad \text{or} \quad \frac{w\lambda}{T_m} = \frac{nE_{T_m}}{2T_m}.$$

Generally E_{T_m}/T_m has a value a little less than $R=1.96$, the gas constant referred to one gram atom, the calorie being the unit of heat. This simple relation has been shown by the present writer* to be satisfied in the case of all metals in which λ and ν are known.

In the above view it is assumed that in the liquid phase even the mono-atom has two or three degrees of freedom for

* K. Honda, Sci. Rep. vii. p. 123 (1918); Phys. Rev. xii. p. 425 (1918).

rotation. This assumption is, however, quite natural, because, according to the electron theory, the atom itself has a very complicated structure, being quite different in shape from a sphere; but in a gaseous phase, the atomic distance being very large as compared with its dimensions, such an atom may behave like a sphere.

If the melting-point of a substance is sufficiently high to admit the equipartition of energy, we have then

$$E_{T_m} = R T_m;$$

hence the total energy of the substance at a temperature T above its melting-point is

$$W = 3RT_m + \frac{1}{2}nRT + Q + 3R(T - T_m)(1 - e),$$

where e has the value lying between 0 and $\frac{1}{2}$; for, if each atom in the liquid phase is making a simple vibration as in the case of the solid phase, we must have $e = 0$. On the other hand, if the temperature be so high that each atom has a translational motion like a gas molecule—that is, in its almost entire length of the free path each atom has a uniform translational motion, and only in very short trips at both ends a retarded or accelerated motion,—then the energy of translational motion for three degrees of freedom is $\frac{3}{2}RT$, and not $3RT$ as in the case of a simple vibration; hence in this case we have $e = \frac{1}{2}$. In the actual case, each atom in the liquid phase has a rectilinear motion of a kind lying between the above two cases, and hence $0 < e < \frac{1}{2}$.

The atomic heat at constant volume in the liquid phase is then

$$C_v = \frac{dW}{dT} = 3R(1 - e) + \frac{1}{2}nR.$$

Hence the values of C_v lie in the following ranges :—

$$\begin{array}{ccc} n = & 2, & 3, \\ C_v = & 4.95-7.92, & 5.94-8.91. \end{array}$$

Since e may increase very slightly with the rise in temperature, C_v is almost independent of temperature, and in some cases slightly decreases with it.

If C_v' be the atomic heat in the solid phase at the melting-point, we have

$$C_v - C_v' = R\left(\frac{n}{2} - 3e\right),$$

which is the change of atomic heat during melting. This difference has a positive or negative value according to the nature of the substance.

The above conclusions agree with the facts experimentally found*.

* I. Iitaka, Sci. Rep. viii p. 99 (1919).

XVI. *On Castigliano's Theorem of Least Work, and the Principle of St. Venant.* By R. V. SOUTHWELL*.

[From the National Physical Laboratory.]

Introduction and Summary.

1. A "FRAMEWORK" is a skeletal structure, designed to transmit through its component members a system of external forces applied at its joints. We shall assume in this paper that every member would be free to turn about either of its ends if the other end were released. Under these conditions, the action in each member must be a pure tension or compression: it is an ideal which practical design seeks generally to attain, since the material can thus be used to the best possible advantage.

A "simple framework" is one which would collapse if any single member were removed: that is to say, it has sufficient members, but no more, to maintain the relative positions of its joints. When the number of members is more than sufficient for this purpose, the structure is termed "redundant". Sometimes it will happen that a framework, although apparently redundant, includes several members which are too flexible to withstand any appreciable compression, and that enough of these go out of action, under the load-system considered, to make it, in effect, simple: the framework is then said to be "pseudo-redundant".

In a redundant framework, it is often convenient to distinguish between two sets of members—the first consisting of "essential members", sufficient by themselves to maintain the position of every joint, and the second of "redundant members". Such classification will of course be largely arbitrary.

2. Redundancy has several important consequences. From the definition of a simple framework it follows that the actions in its members can be found, in terms of the applied loads, from statical considerations alone; in a redundant framework the actions depend also upon the elastic properties of the members. Again, if the external forces be removed from a simple framework, no stress will be left in any member; in a redundant framework, stresses can occur independently of the external loads, by "self-straining", if the length of any redundant member, before insertion in the framework, is not exactly equal to the distance between the joints which it has to connect. Self-straining is often imposed deliberately, by means of turnbuckles, etc., which

* Communicated by the Author.

enable the lengths of redundant members to be altered after insertion. In this way (since a wire which is initially tensioned can function, until its tension is entirely annulled, as a strut), a pseudo-redundant framework can be rendered truly redundant, and its stiffness thereby increased.

From the practical standpoint, a redundant framework has the disadvantage that the stresses in its members are harder to calculate, and the results (for the reasons indicated) less reliable; but for some purposes, and especially in aircraft, its increased stiffness is a more than compensating advantage. Although in the ideal framework the joints are assumed to be free, yet in practice such freedom is often difficult to ensure, and in rigid airships, for example, the joints are more or less rigidly "fixed". Under these conditions, the greater the flexibility of the structure the greater are the racking actions imposed upon the joints, which are almost always points of weakness. For these and other reasons, the problem of calculating stresses in redundant structures is increasing in practical importance.

3. The obvious and direct method of attack is to "compare displacements"*. Considering the simple framework formed by the "essential" members, we can calculate its deflexion under the given load-system, and the additional displacements which result when a specified force is imposed upon it by any one of the redundant members. Hence, regarding the actions in the redundant members as unknowns, and making use of the condition that the extension of any redundant member must be equal to the relative displacement of the joints which it connects, we can obtain sufficient equations for a solution.

This method is (theoretically) applicable, even though the load-extension relations for the members are not expressed by Hooke's law. It has the disadvantage, however, that the calculation of displacements (at all events in a three-dimensional framework) is a lengthy and troublesome operation. A systematic process for effecting this, in structures which satisfy Hooke's law, was described by Clerk Maxwell, in a paper communicated to this Magazine in 1864†; but the method, in spite of

* The practical application of this method has been fully described by W. S. Farren, "The Calculation of Stresses in a Redundant Structure by the Method of Comparison of Deflexions, etc.", *Aeronautical Research Committee*, R. and M. 769.

† "On the Calculation of the Equilibrium and Stiffness of Frames", *Phil. Mag.* vol. xxvii. pp. 294-299. Owing, probably, to the extremely condensed exposition employed, this paper attracted little notice until the method had been rediscovered by Mohr in 1885. Cf. the preface to Mr. Farren's paper (*loc. cit.*), contributed by Prof. H. Lamb.

its formal elegance, involves very serious labour in practice, and redundant frameworks having extension in three dimensions are more usually treated by a method which depends upon Castigliano's celebrated "Theorem of Least Work". For present purposes, this may be stated as follows:—*In a framework which is not initially self-strained, the stresses imposed by a given system of external forces may be found from the conditions for a minimum value of the total strain-energy, if account be taken of the conditions of equilibrium.* It is restricted to structures which obey Hooke's law.

The great merit of this theorem, from a practical standpoint, is that it enables us to dispense with any detailed consideration of displacements. In the equations of equilibrium we have, of course, to deal with forces and actions as vector quantities; but this is a comparatively simple matter, and the subsequent calculations are concerned only with energy,—i. e., with scalar quantities.

4. Castigliano's first statement of his theorem appeared in a thesis for the diploma of engineering at Turin, in 1873. The proof consisted simply in a direct comparison of calculated results.

In a subsequent memoir * he showed that the theorem is a direct corollary of another (also contained in his thesis of 1873), which may be stated thus:—*If the total strain-energy stored in a framework be expressed as a function of the external forces, then the partial differential coefficient of this function with respect to any one of the forces gives the relative displacement of the joint at which that force is applied* †. If the action in any one redundant member be regarded as an external force applied to the remainder of the framework, this theorem gives the expression

$$\delta_1 = \frac{\partial V_1}{\partial P} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

for the relative approach of the joints which are connected by the member considered: P denotes the tension in the member, and V_1 the total strain-energy stored in all the remaining members. In the same way, if we regard

* "Nuova teoria intorno all' equilibrio dei sistemi elastici," Trans. Acad. Sci. Turin, vol. x. (1875), pp. 380-423.

† A proof of this theorem, generally known as the "First Theorem of Castigliano", is given below (§ 12).

the action P as an external force applied to the member in question, and denote the strain-energy stored in this member by V_2 , we obtain the expression

$$\delta_2 = \frac{\partial V_2}{\partial P} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

for its extension under load. Hence, if the member, before insertion in the unstrained framework, was short by an amount λ of the length required to enable it to fit into place, then the condition which must be satisfied, when the member is fitted and the forces applied, is

$$\begin{aligned} \lambda &= \delta_1 + \delta_2, \\ &= \frac{\partial}{\partial P}(V_1 + V_2), \\ &= \frac{\partial V}{\partial P}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3) \end{aligned}$$

where V denotes the strain-energy stored in the complete framework. If the framework was unstrained before the given load-system was applied, λ is zero in this equation, and it may be interpreted as one of the conditions for a minimum value of the total strain-energy V . Corresponding to every unknown tension P we have one equation of the type (3), and a solution can therefore be obtained.

This argument was extended in a treatise (*'Theorem de l'Equilibre des Systèmes Elastiques et ses Applications'*) published in 1879*. By writing equation (3) in the equivalent form

$$\frac{\partial}{\partial P} \{V - \Sigma[\lambda P]\} = 0, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where the summation extends to every redundant member†, Castigliano showed that the stresses in a redundant framework, of which the self-straining is defined by specified quantities of the type λ , may be determined from the

* This treatise has recently been translated by E. S. Andrews (*'Elastic Stresses in Structures'*, 1919). Since the original edition is somewhat scarce, all references in this paper have been made to the English edition: the foregoing historical notes have been taken from Castigliano's preface and from Chap. I. of the translation.

† It can equally be taken as extending to *every* member, since λ is zero for each "essential member".

condition for a minimum value of the quantity

$$V - \Sigma[\lambda P], \dots \dots \dots (5)$$

if account be taken of the conditions of equilibrium. This theorem obviously embraces the Theorem of Least Work.

He showed, further, that analogous theorems hold in respect of the stresses in a continuous elastic solid*. Similar generalization is permissible in regard to the arguments of this paper: it is only for the sake of simplicity that the detailed calculations have been confined to frameworks with free joints.

5. While the advantages of the "Method of Least Work", in problems relating to redundant frameworks, are now generally recognized, there is a widespread feeling that the theorem underlying it is distinctly artificial, and its principles hard to understand†. An alternative proof of the theorem, on physical rather than mathematical lines, may therefore be of interest. In Castigliano's proof, the idea of a minimum appears merely in the mathematical interpretation of equations obtained by comparing displacements, and the device by which equation (3) is thrown into the form (4) is even more artificial. In the argument now advanced, the tendency of the stored strain-energy towards a minimum appears rather as an essential property of materials which obey Hooke's law. Further, if the existence of this property be admitted, it is shown that the well-known "Principle of St. Venant" follows as an immediate corollary.

The argument falls into two parts. In the first, Castigliano's theorems are shown by general reasoning to follow directly from the two principles (i.) of superposition and (ii.) of conservation of energy: at the suggestion of Prof. H. Lamb, a simple illustrative example has been added at each stage of the argument. In the second, these conclusions are confirmed by exact analysis.

The author desires to acknowledge his indebtedness to Prof. B. M. Jones, at whose suggestion this paper was written, and to Prof. H. Lamb, to whom, as on many former occasions, he is indebted for kindly criticism and valuable advice.

* "A general proof is in fact at once obtained if we regard the symbols in his equations as standing for generalized coordinates instead of extensions of bars" (H. Lamb, *loc. cit.*).

† Cf. W. S. Farren, *loc. cit.* p. 7, and the preface by Prof. H. Lamb.

PART I.

An Alternative Proof of the Theorem of Least Work.

6. It should be emphasized at the outset that Castigliano's theorems depend upon the validity of Hooke's law, as an expression not only of the stress-strain relations for each element of the material, but also of the load-extension relation for each member as a whole *. If this requirement is satisfied, the principle of superposition is an immediate consequence: that is to say, any given load-system applied to a framework, and in equilibrium, will increase the actions in the different members and the relative displacements of the joints by amounts which are independent of the stresses already existent. It is immaterial whether these stresses are due to external forces or to self-straining †.

Hence, if all the forces of the system are increased in any constant proportion, the corresponding internal stresses and the displacements of the joints will increase in the same ratio. Again, if these increases occur in a slow and continuous manner, so that equilibrium is established at every stage, and if the system comprises all the external forces which act upon the framework ‡, the work done by each force will be measured by the product of its final value and of half the final displacement, along its line of action, of the joint at which it acts. The total work done on the framework will thus be unaffected by any stresses which may initially exist in it as a consequence of self-straining.

By the principle of conservation of energy, the work thus done by the applied forces must all be stored as strain-energy in the framework. If, then, we write

$$V = V_0 + V', \quad (6)$$

where V_0 denotes the total strain-energy stored in a framework *before* the given load-system is applied, and V the total strain-energy *after* the system is applied, our argument

* Caution is therefore necessary in dealing with structures in which the same member acts both as a compression member of the framework and as a girder transmitting laterally-applied loads to the joints: in such a member, the relation between end-load and total extension may be only approximately expressed by Hooke's law, even when this law represents the relation between the stress and strain in every component element. Cf. A. J. S. Pippard, "The Reduction of the Effective Value of Young's Modulus in Flexible Compression Members". Aeronautical Research Committee, R. and M. 792.

† Cf. § 10.

‡ If other forces act initially, they also will do work as the loads of the given system are increased, and the argument will be modified accordingly.

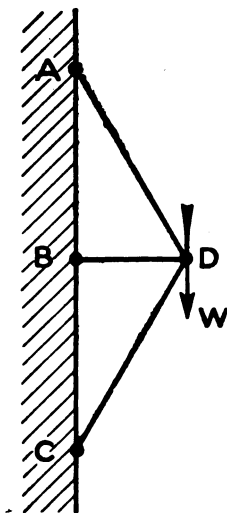
shows that V' , the total increase due to the applied load-system, depends only on that system and on the elastic properties of the framework: it is independent of V_0^* .

Now V_0 , V' , and V , in the nature of the case, are essentially positive quantities; hence, if V' be given, the value of V is least when V_0 is zero. In other words, a framework which is initially unstrained will have less strain-energy stored in it when subjected to any definite load-system than it would have if self-strained to begin with.

But this, in effect, is the Theorem of Least Work. For an expression obtained by means of the conditions of equilibrium, for the total strain-energy in terms of the actions in the redundant members, will obviously embrace every stress-system which can occur in the framework under given applied forces, when no restriction is imposed upon the nature and amount of the initial self-straining; and the result just established shows that the conditions for a minimum value of this expression will yield the correct solution for a framework which is initially unstrained.

A simple example will serve to illustrate the identity stated in (6). In fig. 1, the members DA, DB, DC are

Fig. 1.



connected by smooth joints to the rigid wall ABC: they are assumed to be of uniform material and cross-section, such

* Cf. § 13.

that the member BD, which is 100 ins. long, would extend by $\frac{1}{10}$ in. under a tension of 1000 pounds weight, and the members AD and CD, which are 200 ins. long, by twice that amount. It is easily verified that the self-straining involved when BD is initially short by $\frac{2}{10}$ in. consists of 100 pounds tension in BD, together with compressions of the same amount in AD and CD; also, that a load of W pounds applied at D, as shown, will introduce a tension of $W/\sqrt{3}$ pounds in AD and an equal compression in CD, leaving BD unstrained.

Then if BD is initially short by the unknown amount x ins., the energy stored by self-straining only is as follows:—

in BD,

$$\frac{1}{2} \times 2000x \times \frac{2x}{10} = 200x^2 \text{ in.-pounds ;}$$

in AD or CD,

$$\frac{1}{2} \times (-2000x) \times \left(-\frac{4x}{10}\right) : \text{Sum} = 800x^2 \text{ in.-pounds.}$$

$$\text{Total} = 1000x^2 \text{ in.-pounds} = V_0.$$

When the load W is added, the strain-energy is altered as follows:—

in BD,

$$\frac{1}{2} \times 2000x \times \frac{2x}{10} = 200x^2 \text{ in.-pounds, as before;}$$

in AD,

$$\frac{1}{2} \times \left(\frac{W}{\sqrt{3}} - 2000x\right)^2 \times \frac{2}{10^4},$$

in CD,

$$\frac{1}{2} \times \left(-\frac{W}{\sqrt{3}} - 2000x\right)^2 \times \frac{2}{10^4} :$$

$$\left. \begin{array}{l} \text{Sum} = \frac{2W^2}{3 \times 10^4} + 800x^2 \\ \text{in.-pounds.} \end{array} \right\}$$

$$\begin{aligned} \text{Total} &= \frac{2W^2}{3 \times 10^4} + 1000x^2 \\ &= V. \end{aligned} \text{ in.-pounds,}$$

Thus the increase $V' = V - V_0 = \frac{2W^2}{3 \times 10^4}$ in.-pounds,—a quantity independent of x (or of V_0).

Extension to Frameworks which are Initially Self-Strained.

7. Similar reasoning can be employed to establish Castigliano's theorem in its general form. By the principle of superposition, if the redundant members of a framework be lengthened by definite amounts (*e.g.*, by relaxing the turnbuckles mentioned in § 2), the tension in every member will be reduced by an amount which does not depend either upon the initial self-straining or upon the external forces. But if the framework was initially unloaded, and self-strained to an extent which is exactly neutralized when the redundant members are lengthened by the specified amounts, the tension in every member will be reduced to zero. Hence, in the self-strained framework, if the redundant members are lengthened by amounts $\lambda_1, \lambda_2, \dots$ etc., the tensions in the members will be reduced by amounts $P_0, \dots$ etc., where $P_0, \dots$ etc. are the tensions induced by self-straining when the framework is unloaded and the redundant members "short" (as described in § 4) by the amounts $\lambda_1, \lambda_2, \dots$ etc.

Let us now imagine that we are given the forces applied to a framework, and the amounts, $\lambda_1, \lambda_2, \dots$ etc., by which the redundant members are initially "short". Using the conditions of equilibrium, we can calculate the action in every member in terms of the applied forces and of the actions in the redundant members, and a corresponding expression for the total strain-energy V is at once obtainable; for if we denote the tension in any member by P , and define its elastic properties by means of the equation

$$P = \Omega l^3 e \quad \dots \dots \dots (7)$$

(where Ω is a constant for the member *, l its length, and e its extension under the tension P), we have

$$V = \Sigma \left[\frac{1}{2} P e l \right] = \frac{1}{2} \Sigma \left[\frac{P^2}{l^2 \Omega} \right], \quad \dots \dots \dots (8)$$

the summation extending to every member of the framework.

If we now lengthen the redundant members by amounts equal to our specified values of $\lambda_1, \lambda_2, \dots$ etc., the tension in any member will be reduced, as shown above, by a definite amount P_0 . After this operation, the total strain-energy will therefore be given by

$$V'' = \frac{1}{2} \Sigma \left[\frac{(P - P_0)^2}{l^2 \Omega} \right]. \quad \dots \dots \dots (9)$$

* Cf. equation (12), § 9, and footnote.

As in § 6, the expression obtained for V , since it contains the actions in the redundant members as unknowns, will embrace every stress-system which can occur in the framework, under the given forces, when no restriction is imposed upon the nature and amount of the initial self-straining. The expression (9) is equally general. But if the correct values are inserted for the actions in the redundant members, so that (8) corresponds to the correct system of self-straining, then after the redundant members have been lengthened the framework will be entirely free from self-straining, and hence, by the Theorem of Least Work, the total strain-energy stored in it when subjected to the given load-system will have its least possible value. We can therefore derive the correct solution from the conditions for a minimum value of V'' .

The form of the expression (9) is not a convenient one for this calculation, since we should require to know $P_0, \dots$ etc. in terms of $\lambda_1, \lambda_2, \dots$ etc. We therefore investigate an alternative expression for the quantity $(V - V'')$. By the principle of conservation of energy, this quantity must be equal to the work gained in the operation of increasing the lengths of the redundant members, less the work done during this operation by the external forces; for the work stored by the external forces (and recoverable by removing them) will be unchanged. The tension in any one of the redundant members is represented by P at the start and by $(P - P_0)$ at the finish, so that its mean value during the operation is $(P - \frac{1}{2}P_0)$: hence, the work gained in lengthening this member is $(P - \frac{1}{2}P_0)\lambda$. Again, if $u, v, w, \dots$ are the displacements of the joints from the zero configuration* when the framework is self-strained to an extent defined by $\lambda_1, \lambda_2, \dots$ etc., and if $\bar{X}, \bar{Y}, \bar{Z}, \dots$ etc. are the external forces acting on the framework, the total work done by these forces in the operation (which *reduces* the displacements by amounts $u, v, w, \dots$) will be given by the expression

$$-\Sigma[uX + v\bar{Y} + wZ],$$

in which the summation extends to every joint.

We thus obtain the expression

$$V - V'' = \Sigma_m[(P - \frac{1}{2}P_0)\lambda] + \Sigma_j[uX + v\bar{Y} + wZ], \quad (10)$$

in which Σ_m denotes a summation extending to every member, and Σ_j a summation extending to every joint.

* *I.e.*, from their positions in the simple and unstrained framework formed by the "essential members" only. Cf. § 9.

But the terms on the right of (10), excepting those of type $P\lambda$, are invariant, since they depend only upon the external forces and upon $\lambda_1, \lambda_2, \dots$ etc. Hence, the conditions for a minimum value of V'' are the conditions for a minimum value of the quantity

$$V - \Sigma [P.\lambda] : \dots \dots \dots (11)$$

and since this is the quantity similarly denoted in equation (5), we have obtained an alternative proof of Castigliano's theorem in its application to self-strained frameworks.

The relation expressed by (10) may be illustrated by means of the example previously considered. Suppose, as before, that BD is initially short by the unknown amount x inches, and that a load of W pounds weight is applied at D; and let us imagine that BD is now relaxed (*i.e.*, lengthened) by $\frac{1}{20}$ inch. The effect is to superpose a compression of 100 pounds in BD and tensions of equal magnitude in AD and CD, whence the strain-energy stored after the operation is as follows :—

in BD,

$$200(x - \frac{1}{20})^2 = 200x^2 - 20x + \frac{1}{2} \text{ in.-pounds ;}$$

in AD,

$$\frac{1}{10} \times \left(\frac{W}{\sqrt{3}} - 2000x + 100 \right)^2,$$

in CD,

$$\frac{1}{10} \times \left(-\frac{W}{\sqrt{3}} - 2000x + 100 \right)^2 :$$

$$\left. \begin{array}{l} \text{Sum} = \frac{2W^2}{3 \times 10^4} + 800x^2 - 80x + 2 \\ \text{in.-pounds.} \end{array} \right\}$$

$$\begin{aligned} \text{Total} &= \frac{2W^2}{3 \times 10^4} + 1000x^2 - 100x + \frac{5}{2} \\ &= V'' \end{aligned}$$

It follows that

$$V - V'' = 100x - \frac{5}{2} \text{ in.-pounds.}$$

But the tension in BD was $2000x$ pounds at the start and $(2000x - 100)$ pounds at the finish, so that $P = 2000x$ and $P_0 = 100$; also $\lambda = \frac{1}{20}$. Hence we have

$$(P - \frac{1}{2}P_0)\lambda = (2000x - 50) \times \frac{1}{20} = 100x - \frac{5}{2} = V - V''.$$

and the relation (10) obtains, since in this example no work

is done by the force W during the process of lengthening BD .

The effect of lengthening AD or CD may be investigated in the same way : it will be found that (10) is still satisfied, although work is here done by W .

A Physical Basis for the Principle of St. Venant.

8. If in the foregoing proof of Castigliano's theorem we regard the symbols as standing for generalized coordinates *, it appears that the stresses in any elastic solid which obeys Hooke's law will adjust themselves, under a given system of applied tractions, so that the total strain-energy stored by those tractions has the least value consistent with the satisfaction of the conditions of equilibrium.

If we regard this tendency as in the nature of a physical property of the material, we may find in it the basis of the principle, due to St. Venant, which is known as the "Elastic Equivalence of Statically Equipollent Systems of Load". According to this principle †, which is widely utilized in the theory of elasticity, the strains which are produced in a body by the application, to a small part of its surface, of a system of forces statically equivalent to zero force and zero couple are of negligible magnitude at distances which are large compared with the linear dimensions of the part ; hence, by the principle of superposition, it may be inferred that *forces applied at one part of an elastic structure will induce stresses which, except in a region close to that part, will depend almost entirely upon their resultant action, and very little upon their distribution.*

St. Venant's principle appears to have been originally propounded, and to have remained since, without proof. But the theorem just stated in italics may be regarded as an immediate consequence of the tendency towards a minimum storage of strain-energy. Let us consider the case of a long girder, or braced framework, which is loaded at its two ends by forces applied in any given way ; and let us employ the symbol A to denote those regions which immediately adjoin the parts at which the forces are applied, and the symbol B for the remainder. The conditions of equilibrium requires merely that the resultant action transmitted by B shall have a definite

* Cf. § 4 and footnote.

† Cf. A. E. H. Love, 'Mathematical Theory of Elasticity', § 89.

value; but the conditions of continuity (or of compatibility of strains) will not be satisfied unless the total increase of the strain-energy stored in A and B has its minimum value. Evidently, then, the equilibrium configuration may be regarded as in the nature of a compromise between the requirements of A and B. To reduce to a minimum the strain-energy stored in A, the reactions between A and B would require to distribute themselves in a manner which will depend upon the distribution of the forces applied to A; the requirements of B, on the other hand, will not vary, since there must be some definite distribution of stresses, in an otherwise unloaded body, which will entail the minimum storage of strain-energy in transmitting a given resultant action.

Thus, in the process of adjustment which results in the actual distribution corresponding to equilibrium, we may picture a contest between the unloaded portions*, which strive always after "standardization", and the loaded portions, which demand a particular solution for every specified distribution of the forces acting on them. As we pass from the regions of application of load through successive sections of the unloaded portion B, there will be a steady tendency for the claims of standardization to prevail. The theorem stated in italics is an immediate deduction, and we may work back from this, by the principle of superposition, to St. Venant's Principle.

One final remark may be made in this connexion. If our long girder or fuselage is of uniform construction, the requirements of every elementary slice of the unloaded portion, as regards the distribution of stress over its faces which will make the stored strain-energy a minimum, must be the same. We can thus see a physical reason for the predominance of the solutions which St. Venant obtained on the assumption that the stresses are transmitted, in a uniform prism, without change of type: for these must be the "least-energy" solutions for a uniform prism with free surfaces, and as such will be the standard systems to which all particular stress-systems must tend, as we pass from the regions in which the external forces are applied.

* *I.e.*, portions of which the external surfaces are free from load.

PART II.

Notation, etc.

9. The remainder of this paper will be concerned with exact analytical proofs of relations which we have previously inferred from physical considerations.

As stated already (§ 6), it is essential that Hooke's law be an expression of the load-extension relation for each member as a whole. We shall find that our equations can be simplified by writing them in terms of "tension-coefficients"*, which we denote by the symbol T : the tension-coefficient for any member is defined as the total tension in that member, divided by its length. In the notation of equation (7), we have then

$$P = Tl = \Omega l^3 e, \quad (12)$$

where Ω is a constant which conveniently defines the elasticity of the member in question†; and if v denotes the strain-energy stored in any member when it is extended by a tension of magnitude P , we have

$$\left. \begin{aligned} v &= \frac{1}{2} Ple = \frac{1}{2} T l^2 e, \\ &= \frac{1}{2} \frac{P^2}{l^2 \Omega} = \frac{1}{2} \frac{T^2}{\Omega}. \end{aligned} \right\} (13)$$

The total strain-energy stored in a framework may thus be expressed in the form

$$\left. \begin{aligned} V &= \Sigma [v], \\ &= \frac{1}{2} \Sigma \left[\frac{P^2}{l^2 \Omega} \right] = \frac{1}{2} \Sigma \left[\frac{T^2}{\Omega} \right], \end{aligned} \right\} (14)$$

the summation extending to every member.

In the notation of "tension-coefficients", the equations

* Cf. the author's paper on "Primary Stress-Determination in Space Frames", 'Engineering', Feb. 6th, 1920.

† Cf. R. and M. 737 of the Aeronautical Research Committee, § 4. In a member of uniform cross-section A , and composed of material of which the Young's Modulus is E , we have

$$\Omega = \frac{EA}{l^3};$$

the modifications required for taking account of varying cross-section or material are obvious.

of equilibrium for any joint A of the framework take the form *

$$\left. \begin{aligned} X_A &= T_{AB}(x_A - x_B) + T_{AC}(x_A - x_C) + \dots, \\ Y_A &= T_{AB}(y_A - y_B) + T_{AC}(y_A - y_C) + \dots, \\ Z_A &= T_{AB}(z_A - z_B) + T_{AC}(z_A - z_C) + \dots, \end{aligned} \right\} \quad (15)$$

where X_A , Y_A , Z_A are the components, in the directions of x , y and z respectively, of the external force acting at A, and T_{AB} , T_{AC} , ... etc. are the tension-coefficients for the members, AB, AC, ... etc., which connect the joint A to other joints of the framework.

Let u_A , v_A , w_A denote the component displacements of the joint A, in the directions of x , y and z respectively, from its position in the "zero configuration",—i. e., in the simple and unstrained framework formed by the "essential members" only. Then the fractional increase in the distance between any two joints A and K is given by †

$$\frac{(x_A - x_K)(u_A - u_K) + (y_A - y_K)(v_A - v_K) + (z_A - z_K)(w_A - w_K)}{l_{AK}^2}.$$

Suppose now that the joints A and K are joined by one of the members classified as redundant, and that before insertion this member is "short" by the quantity λ_{AK} of the distance between A and K in the zero configuration. Then, when this member is in place, and the joints A and K have undergone displacements u_A , v_A , w_A , u_K , v_K , w_K , its fractional extension will be given by the expression

$$e_{AK} = \frac{\lambda_{AK}}{l_{AK}} + \frac{(x_A - x_K)(u_A - u_K) + (y_A - y_K)(v_A - v_K) + (z_A - z_K)(w_A - w_K)}{l_{AK}^2}, \quad (16)$$

from which the tension-coefficient for AK may be calculated by means of (12), and inserted in the equations (15) of equilibrium. The expression (16) is clearly applicable to "essential" as well as to "redundant" members, the quantity λ_{AK} being zero for a member of the former type.

* Cf. 'Engineering', *loc. cit.*, equations (2)-(4).

† Cf. R. and M. 737, equation (2).

The extensions, as usual, are assumed to be so small that their products may be neglected. It is then a matter of indifference whether l_{AK} , in (16), represents the strained or unstrained length of the member AK , or the distance between the joints A and K in the zero configuration.

Proof of the Principle of Superposition (§6).

10. In a framework of any specified dimensions, let $u, v, w, \dots$ denote the displacements of the joints from the zero configuration, after equilibrium has been established under a load-system defined by $X, Y, Z, \dots$ etc., when the redundant members are initially short by the amounts $\lambda_{AK}, \dots$ etc. And let $u', v', w', \dots$ denote the corresponding displacements for a load-system defined by $X', Y', Z', \dots$, when the redundant members are initially short by the amounts $\lambda'_{AK}, \dots$ etc. Then it can be seen at once, from the linearity of the equations (12), (15) and (16), that $(u+u'), (v+v'), (w+w'), \dots$ will constitute a solution for the displacements corresponding to a load-system defined by $(X+X'), (Y+Y'), (Z+Z'), \dots$ etc., when the redundant members are initially short by the amounts $(\lambda_{AK} + \lambda'_{AK}), \dots$ etc.

It follows (if we make $\lambda'_{AK}, \dots$ etc. severally zero) that the effect of applying any definite load-system $X'_A, Y'_A, Z'_A, \dots$ etc., or (if we make $X'_A, Y'_A, Z'_A, \dots$ etc. severally zero) the effect of relaxing our "redundant" members by any definite amounts, is to produce the same increments in the displacements and tensions, whatever be the load-system and self-straining existent initially. This is the Principle of Superposition.

A Reciprocal Theorem.

11. Let $T_{AK}, \dots$ etc. denote the tension-coefficients for the members of a given framework, when the initial self-straining is defined by $\lambda_{AK}, \dots$ etc. and the external loads are $X_A, Y_A, Z_A, \dots$ etc. And let $T'_{AK}, \dots$ etc. denote the tension-coefficients for the same framework, when the initial self-straining is defined by $\lambda'_{AK}, \dots$ etc. and the external loads are $X'_A, Y'_A, Z'_A, \dots$ etc. We shall derive alternative expressions for the quantity

$$\Sigma \left[\frac{T \cdot T'}{\Omega} \right], \dots \dots \dots (17)$$

in which the summation extends to every member of the framework.

Let the displacements from the "zero configuration", under the first conditions, be denoted by $u_A, v_A, w_A, \dots$ etc. Then we have, from (12) and (16),

$$\frac{T_{AK}}{\Omega_{AK}} = l_{AK} \cdot \lambda_{AK} + \{(x_A - x_K)(u_A - u_K) + (y_A - y_K)(v_A - v_K) + (z_A - z_K)(w_A - w_K)\}. \quad (18)$$

Making this substitution in (17), we have, corresponding to the first term on the right of (18), the quantity

$$\Sigma[l\lambda T'], \quad \dots \quad (19)$$

in which the summation extends to every member. The summation corresponding to the second term on the right of (18) may be arranged in the alternative form

$$\Sigma \left[\begin{array}{l} u_A \{ (x_A - x_B)T'_{AB} + \dots + (x_A - x_K)T'_{AK} + \dots \} \\ + v_A \{ (y_A - y_B)T'_{AB} + \dots + (y_A - y_K)T'_{AK} + \dots \} \\ + w_A \{ (z_A - z_B)T'_{AB} + \dots + (z_A - z_K)T'_{AK} + \dots \} \end{array} \right], \quad (20)$$

where, in the series enclosed by twisted brackets, terms are included for every member which connects the joint A with another joint. The summation in (20) extends to every joint.

But the equations of equilibrium, which are of the type (15), show that (20) may be written in the form

$$\Sigma[uX' + vY' + wZ'],$$

the summation extending to every joint. Hence, and by (19), we have

$$\begin{aligned} \Sigma_m \left[\frac{T \cdot T'}{\Omega} \right] &= \Sigma_m[l\lambda T'] + \Sigma_j[uX' + vY' + wZ'] \\ &= \Sigma^m[l\lambda' T] + \Sigma_j[u'X + v'Y + w'Z], \quad (21) \end{aligned}$$

by symmetry, where suffixes m and j attached to Σ denote summations with respect to every member, and to every joint, respectively.

These alternative expressions for the same quantity give
Phil. Mag. S. 6. Vol. 45. No. 265. Jan. 1923. P

us a reciprocal relation between any two configurations which can be maintained in a given framework. As a particular example, we may suppose that the self-straining in both configurations is zero. Then $u, v, w, \dots$ etc. represent the additional displacements of the joints which result from an application of the load-system $X, Y, Z, \dots$, and u', v', w' represent the additional displacements which result from an application of the load-system $X', Y', Z', \dots$, etc. Equations (21) now give the relation

$$\begin{aligned}\Sigma_m \left[\frac{T \cdot T'}{\Omega} \right] &= \Sigma_j [X'u + Y'v + Z'w] \\ &= \Sigma_j [Xu' + Yv' + Zw'], \quad \dots \quad (22)\end{aligned}$$

which is Lord Rayleigh's reciprocal theorem*.

Castigliano's First Theorem (§ 4).

12. If we identify the two systems considered in (22), we obtain, as an expression for the strain-energy stored by forces $X', Y', Z', \dots$ applied to a framework which is not initially self-strained,

$$V = \frac{1}{2} \Sigma_m \left[\frac{T'^2}{\Omega} \right] = \frac{1}{2} \Sigma_j [X'u' + Y'v' + Z'w']. \quad (23)$$

Let $\delta u', \delta v', \delta w', \dots$ etc. denote the increments of displacement, and $\delta V'$ the increment of strain-energy, resulting from increments $\delta X', \delta Y', \delta Z', \dots$ made in the applied loads. Regarding all these increments as small quantities, and neglecting small quantities of the second order, we have then, from (23),

$$\begin{aligned}\delta V &= \frac{1}{2} \Sigma_j [\delta X' \cdot u' + \delta Y' \cdot v' + \delta Z' \cdot w'] \\ &\quad + \frac{1}{2} \Sigma_j [X' \cdot \delta u' + Y' \cdot \delta v' + Z' \cdot \delta w']. \quad (24)\end{aligned}$$

But if, in (22), we identify the undashed quantities with the increments now considered, we have

$$\begin{aligned}\Sigma_j [X' \cdot \delta u' + Y' \cdot \delta v' + Z' \cdot \delta w'] \\ = \Sigma_j [\delta X' \cdot u' + \delta Y' \cdot v' + \delta Z' \cdot w'].\end{aligned}$$

Making use of this result in (24), and assuming that all the increments in the applied forces, except one ($\delta X'_A$ say),

* Cf. A. E. H. Love, 'Mathematical Theory of Elasticity', § 121.

are zero, we obtain the relation

$$\delta V = \delta X'_A \cdot u'_A,$$

whence

$$u'_A = \frac{\partial V}{\partial X'_A} \quad \dots \dots \dots (25)$$

This is Castigliano's first theorem.

Increase in Strain-Energy caused by the Application of a given Load-System (§ 6).

13. Equation (23) of the preceding section gives an expression for the total strain-energy stored by a load-system $X', Y', Z', \dots$ applied to a framework which is not initially loaded or self-strained. We can show that this expression will also hold for the *total increase of strain-energy* which results when the same load-system is applied to a framework which is initially self-strained, provided that no external forces act initially. For if, in the equations (21), T, λ, u, v, w represent a configuration of self-straining without external load (so that $X, Y, Z, \dots$ vanish severally), and T', u', v', w' a system due entirely to external loads $X', Y', Z', \dots$ etc. (so that $\lambda', \dots$ vanish severally), we have

$$\begin{aligned} \Sigma_m \left[\frac{T \cdot T'}{\Omega} \right] &= \Sigma_m [l\lambda T'] + \Sigma_j [uX' + vY' + wZ'] \\ &= 0. \quad \dots \dots \dots (26) \end{aligned}$$

Suppose then that the load-system here denoted by $X', Y', Z', \dots$ is applied to the framework when it is self-strained to an extent which is defined by the undashed quantities $T, \dots, \lambda, \dots$. By the principle of superposition, the tension-coefficients have their values increased to $(T+T')$, etc., and the total increase in the strain-energy

$$\begin{aligned} = V' &= \frac{1}{2} \Sigma_m \left[\frac{(T+T')^2}{\Omega} \right] - \frac{1}{2} \Sigma_m \left[\frac{T^2}{\Omega} \right], \text{ by (13),} \\ &= \Sigma_m \left[\frac{T \cdot T'}{\Omega} \right] + \frac{1}{2} \Sigma_m \left[\frac{T'^2}{\Omega} \right], \\ &= 0 + \frac{1}{2} \Sigma_m \left[\frac{T'^2}{\Omega} \right], \text{ by (26).} \end{aligned}$$

The expression (23) is thus unaffected by initial self-straining.

Effect of a Relaxation of the Self-Straining.

14. We have shown in § 10 that a system of self-straining may be superposed or subtracted. Let us define any such system by undashed quantities, and imagine it to be subtracted from a configuration represented by barred quantities ($\bar{u}, \bar{v}, \bar{w}, \bar{\lambda}, \bar{T}, \bar{X}, \dots$ etc.). Then the final value of the total strain-energy is

$$\begin{aligned} V'' &= \frac{1}{2} \Sigma_m \left[\frac{(\bar{T} - T)^2}{\Omega} \right], \\ &= \frac{1}{2} \Sigma_m \left[\frac{T^2}{\Omega} \right] - \Sigma_m \left[\frac{\bar{T} \cdot T}{\Omega} \right] + \frac{1}{2} \Sigma_m \left[\frac{\bar{T}^2}{\Omega} \right]. \quad (27) \end{aligned}$$

Suppose now that the undashed quantities in (21) relate to a system of self-straining only (so that $X, Y, Z, \dots$ etc. vanish identically). Then if we identify the dashed quantities with the undashed, we have

$$\Sigma_m \left[\frac{T^2}{\Omega} \right] = \Sigma_m [\lambda T], \quad . \quad . \quad . \quad . \quad (28)$$

and if we identify them with our barred quantities, we have

$$\Sigma_m \left[\frac{\bar{T} \cdot \bar{T}}{\Omega} \right] = \Sigma_m [\lambda \bar{T}] + \Sigma_j [u \bar{X} + v \bar{Y} + w \bar{Z}]. \quad (29)$$

We may therefore write (27) in the form

$$\begin{aligned} V'' &= V - \Sigma_m [\lambda \bar{T}] + \frac{1}{2} \Sigma_m [\lambda T] \\ &\quad - \Sigma_j [u \bar{X} + v \bar{Y} + w \bar{Z}], \quad (30) \end{aligned}$$

where V denotes the initial value of the total stored strain-energy. This is the result obtained in equation (10) of § 7, since in the notation of that section

$$\begin{aligned} P &= l \bar{T} \\ \text{and} \quad P_0 &= l T. \end{aligned}$$

September, 1922.

XVII. *The Molecular Scattering of Light in Liquid Mixtures.*

By C. V. RAMAN, M.A., Hon.D.Sc., Palit Professor of Physics in the Calcutta University, and K. R. RAMANATHAN, M.A., University of Madras Research Scholar*.

1. *Introduction.*

AS is well known, there are many substances, *e. g.* phenol and water, which in the liquid state dissolve each other completely and form a single phase above a certain temperature, but below it are only partially soluble and divide into two coexistent phases. Such mixtures exhibit a marked opalescence or turbidity at temperatures slightly higher than that at which they separate into two layers. Smoluchowski† put forward a thermodynamic explanation of this phenomenon as due to the spontaneous local fluctuations of concentration which occur in the mixture and cause optical inhomogeneity. The problem was further handled by Einstein‡, who made certain simplifying assumptions, namely, that the liquids are incompressible, that their specific volumes are negligibly small in comparison with those of the saturated vapours emitted by them, and that the latter can be treated as ideal gases, and on this basis derived a formula for the opalescence of the mixture in terms of experimentally determinable magnitudes, that is, the variation of its refractive index and of the partial vapour-pressures of its components with alteration of concentration. The simplifications referred to, however, considerably restrict the validity of the investigation which, in fact, can be regarded as strictly applicable only over a small range of temperature above that at which the mixture separates into two phases. For such a restricted range, the correctness of Einstein's formula has been experimentally established by the investigations of Fürth§ and of Zernike||. Actually, however, by using carefully purified liquids freed from dust by repeated distillation *in vacuo*, the opalescence in mixtures may be studied over any desired range of temperature and not merely in the immediate vicinity of the critical solution point, and very remarkable and interesting changes in the intensity of the scattered

* Communicated by the Authors.

† *Annalen der Physik*, xxv. p. 219 (1908).

‡ *Annalen der Physik*, xxxiii. p. 1295 (1910).

§ *Wiener Sitzungsberichte*, p. 577, 1915.

|| Thèse, Amsterdam, 1915.

light and the state of its polarization are observed. These phenomena are also noticeable in mixtures of liquids which are completely soluble in each other at the ordinary temperature. It is found that Einstein's approximate investigation is not adequate to explain the observed facts in these cases and that a stricter investigation is called for. It is proposed in this paper to show how by a modification of the procedure adopted by Einstein, a *perfectly rigorous* expression for the light-scattering can be derived in terms of experimentally determinable quantities. A comparison is also made between the results of the modified theory and those observed in experiment. Specially noteworthy are the effects arising from *molecular anisotropy* which, of course, are not contemplated at all in Einstein's theory. These are discussed in detail in the course of the paper.

2. *Thermodynamical Theory : Application of Boltzmann's Principle.*

In order to deal with the problem under consideration, Einstein assumed that the refractive index of the mixture is a function of a single variable k which expresses the concentration of the mixture, that is the ratio of the mass of the second component present to that of the first component. This is not, however, correct. We have in reality to deal with *two* independent variables, namely, the densities of both components, and the local fluctuations of refractive index are determined by variations of both of these quantities. One way of determining the accidental deviations of density in a mixture is by applying the principles of statistical mechanics. This has been attempted by Ornstein*. In order, however, to express the results in terms of physically measurable quantities, it is simpler to use a purely thermodynamical treatment based upon Boltzmann's well-known relation between entropy and probability. In order to make use of this principle, we have to find the change of entropy resulting from small increases Δm_1 and Δm_2 in the masses, m_1 and m_2 of the components actually present in unit volume of the mixture. The probability of such deviations occurring spontaneously and their mean value may then be evaluated. In order to find the change of entropy involved we have to imagine the masses Δm_1 and Δm_2 introduced into unit volume of the mixture isothermally and by a reversible process. The following thermodynamical operation, which is a modification of that used by Einstein, enables this to be done.

* Proc. Roy. Soc. Amsterdam, xv. p. 54 (1912).

Consider unit volume of the mixture enclosed in a cylinder fitted with a frictionless piston by which the hydrostatic pressure can be varied. The base of the cylinder has two openings, which may be either closed at will or fitted with membranes permeable respectively to the vapour of the first and second components only. A second and much larger reservoir similarly fitted with a piston and semi-permeable openings is assumed to be filled with the liquid mixture, this being maintained at the same temperature and at a hydrostatic pressure equal to the total vapour pressure ϕ of the mixture. The following isothermal operations may then be carried out.

Stage 1.

By means of auxiliary pumps applied to the semi-permeable openings, small masses (Δm_1) and (Δm_2) of the two components may be removed in the state of vapour from the reservoir, the volume of which is assumed to be so great that no appreciable alteration in the composition of its contents occurs in consequence of this removal.

If p_1 and p_2 be respectively the partial pressures of the vapours and v_1 and v_2 their specific volumes, the work done in the process is

$$-p_1 v_1 \Delta m_1 - p_2 v_2 \Delta m_2 + [s_1 \Delta m_1 + s_2 \Delta m_2] \phi, \quad (1)$$

where s_1 and s_2 represent respectively the shrinkages of the volume of the mixture by removal of unit masses of the two components.

Stage 2.

Taking the masses (Δm_1) and (Δm_2) of the vapours thus separated, force simultaneously a mass (Δm_1) of the first component and a mass ($k \Delta m_1$) of the second component into the cylinder the contents of which are maintained at a constant hydrostatic pressure ϕ , k being the fraction m_2/m_1 . It is clear that in this operation the composition of the mixture, and therefore also its vapour-pressure, remain unaltered. The work done in this process is therefore

$$p_1 v_1 \Delta m_1 + p_2 v_2 k \Delta m_1 - [s_1 \Delta m_1 + s_2 k \Delta m_1] \phi. \quad (2)$$

Stage 3.

Force the remaining portion ($\Delta m_2 - k \Delta m_1$) of the second component into the cylinder, the hydrostatic pressure in it

being maintained at the equilibrium value of its total vapour-pressure at each instant. The work done in this process is

$$v_2(\Delta m_2 - k\Delta m_1)(p_2 + \frac{1}{2}\Delta p_2) - s_2(\Delta m_2 - k\Delta m_1)(\phi + \frac{1}{2}\Delta\phi), \quad (3)$$

where (Δp_2) and $(\Delta\phi)$ represent respectively the changes of the partial vapour-pressure and the total vapour-pressure resulting from the operation.

Stage 4.

The volume of the mixture in the smaller cylinder is now greater than at first by $(s_1\Delta m_1 + s_2\Delta m_2)$. The semi-permeable openings are now closed, and the piston enclosing the contents forced in by increasing the hydrostatic pressure till the original volume is restored. The work done in this process is

$$\frac{1}{2}\beta(\Delta p)^2 \quad \dots \quad (4)$$

where β is the compressibility, of the mixture and (Δp) is the increase of hydrostatic pressure in the process.

Adding up (1), (2), (3), and (4) we find the total work done is

$$\frac{1}{2}(v_2\Delta p_2 - s_2\Delta\phi)(\Delta m_2 - k\Delta m_1) + \frac{1}{2}\beta(\Delta p)^2. \quad \dots \quad (5)$$

The quantity k is a measure of the concentration of the mixture. If it be altered to $k + \Delta k$ as the result of the operations set out above, it is easily seen that $m_1\Delta k = (\Delta m_2 - k\Delta m_1)$.

Hence (5) may be written in the form

$$\frac{1}{2}m_1\left(v_2\frac{\partial p_2}{\partial k} - s_2\frac{\partial \phi}{\partial k}\right)(\Delta k)^2 + \frac{1}{2}\beta(\Delta p)^2,$$

or, for brevity,

$$\frac{1}{2}\alpha(\Delta k)^2 + \frac{1}{2}\beta(\Delta p)^2. \quad \dots \quad (6)$$

The next step is to find the mean value of $(\Delta k)^2$ and $(\Delta p)^2$ in the deviations which occur spontaneously in a volume-element dv of the mixture. We may for this purpose use Boltzmann's principle in the form in which it has been expressed by Einstein,

$$dW = Ce^{-\frac{NE}{RT}} d\lambda_1 d\lambda_2 \dots d\lambda_n, \quad \dots \quad (7)$$

where $\lambda_1, \lambda_2 \dots \lambda_n$ are suitably chosen variables which determine the observable condition of the system and dW is the probability that the magnitudes λ_1, λ_2 , etc., lie between λ_1 and $\lambda_1 + d\lambda_1, \lambda_2$ and $\lambda_2 + d\lambda_2$, etc., R, T , and N have the same significance as in kinetic theory. C is a constant and E is the work necessary to bring the system into the state

under consideration from that of thermodynamical equilibrium. If $\lambda_1, \lambda_2 \dots$ are assumed to be zero in the state of equilibrium and E can be expressed in the form

$$E = \frac{1}{2}a_1\lambda_1^2 + \frac{1}{2}a_2\lambda_2^2 + \dots + \frac{1}{2}a_n\lambda_n^2, \quad \dots \quad (8)$$

then (7) assumes the familiar form of the Gaussian error-law and it may easily be shown by integration that

$$\left. \begin{aligned} \bar{\lambda}_1^2 &= RT/Na_1, \quad \bar{\lambda}_2^2 = RT/Na_2, \text{ etc.}, \\ \bar{\lambda}_1\bar{\lambda}_2 &= \bar{\lambda}_2\bar{\lambda}_3 \dots = 0, \end{aligned} \right\}, \quad \dots \quad (9)$$

where the bars indicate the mean value of the quantities written under them.

Comparing (6) and (8), we find from (9) that for an elementary volume dv of the mixture

$$\left. \begin{aligned} (\overline{\Delta k})^2 &= \frac{RT}{N} \frac{1}{\alpha dv}, \\ (\overline{\Delta p})^2 &= \frac{RT}{N} \frac{1}{\beta dv}, \\ \text{and } \overline{\Delta k} \overline{\Delta p} &= 0. \end{aligned} \right\} \dots \dots \dots (10)$$

Writing $\epsilon = \mu^2$ where μ is the refractive index of the mixture,

$$\Delta\epsilon = \frac{\partial\epsilon}{\partial k} \cdot \Delta k + \frac{\partial\epsilon}{\partial p} \Delta p,$$

and from (10), it follows at once that

$$(\overline{\Delta\epsilon})^2 = \frac{RT}{Ndv} \left[\left(\frac{\partial\epsilon}{\partial k} \right)^2 / \alpha + \left(\frac{\partial\epsilon}{\partial p} \right)^2 / \beta \right]. \quad \dots \quad (11)$$

3. Intensity of the Scattered Light : Comparison with Einstein's formula.

From (11), the intensity of the opalescence radiation can be easily calculated. Using a relation given by the late Lord Rayleigh *, we find that in a direction at right angles to the incident beam (assumed to be unpolarized and of unit intensity), the intensity of the scattered light is

$$I = \Sigma \frac{\pi^2 (dv)^2 (\overline{\Delta\epsilon})^2}{2\lambda^4} / r^2,$$

where λ is the wave-length and r is the distance of the volume-element from the point of observation. Substituting

* Scientific Papers, vol. i. p. 526.

for $(\Delta\epsilon)^2$ from (11), and integrating over the whole volume of the fluid, say Ψ ,

$$I = \frac{\Psi}{r^2} \cdot \frac{\pi^2 RT}{2N\lambda^4} \left[\left(\frac{\partial\epsilon}{\partial k} \right)^2 / m_1 \left(v_2 \frac{\partial p_2}{\partial k} - s_2 \frac{\partial\phi}{\partial k} \right) + \beta \rho^2 \left(\frac{\partial\epsilon}{\partial \rho} \right)^2 \right], \quad \dots (12)$$

where ρ is the density of the mixture.

The principal difference between Einstein's expression for the light-scattering in liquid mixtures and that given here is that the former does not include the term proportional to the compressibility of the mixture which appears in (12). This term expresses the light-scattering due to the local thermal *fluctuations of density* in the mixture considered as a single substance. Using Lorentz's relation $(\epsilon - 1)/(\epsilon + 2) = \text{const.} \rho$, the second term in (12) may be developed and written in the form

$$\frac{\pi^2 RT \beta}{18 N \lambda^4} (\mu^2 - 1)^2 (\mu^2 + 2)^2 \frac{\Psi}{r^2}. \quad \dots (13)$$

The first term in (12) which represents the light-scattering due to the local *fluctuations of concentration* in the mixture may be simplified if we neglect $s_2 \frac{\partial\phi}{\partial k}$ in comparison with $v_2 \frac{\partial p_2}{\partial k}$ and assume, further, that the saturated vapour obeys the gas laws, in which case it may be written as

$$\frac{M_2}{2N\lambda^4} \cdot \frac{1}{m_1} \frac{(\partial\epsilon/\partial k)^2}{\partial \log p_2 / \partial k} \cdot \frac{\Psi}{r^2}, \quad \dots (14)$$

where M_2 is the molecular weight of the second component in the gaseous phase. (14) is Einstein's approximate result. The simplifications here made are only permissible when the vapour-pressure is not large.

The relative importance of the two effects, viz. the light-scattering due to fluctuations of density and concentration respectively, which contribute to its total observed intensity depends on the circumstances of the particular case. The first effect depends on the refractive index and compressibility of the mixture, and second on the variations of refractive index and of the partial vapour-pressures produced by a change in the composition of the mixture. In the immediate neighbourhood of the critical solution temperature,

the partial vapour-pressures alter very little with the composition of the mixture, and the concentration-scattering becomes very great. On the other hand, at temperatures far removed from the critical solution point or in the cases in which the components are ordinarily completely miscible, the partial vapour-pressures change rapidly with concentration, the concentration scattering becomes less, and if the refractive indices of the components do not differ much, it may even become unimportant in comparison with the density scattering. The relative proportion of the two components in the mixture is also of importance. It is evident that when either of the components forms a vanishingly small proportion of the mixture, the concentration-scattering would disappear and the observed opalescence would be due entirely to the density-scattering in the remaining component. The composition of the liquid would also influence the density-scattering, since the refractive index and compressibility of the mixture are both functions of it.

4. *Effect of Molecular Anisotropy.*

The theory so far discussed rests on a purely thermodynamical basis and leads to the result that the light scattered in a direction transverse to the primary beam should be completely polarized. If we had proceeded on the basis of a molecular theory we should have obtained a precisely identical result, provided the molecules could be treated as isotropic or spherical scattering particles exerting forces on each other. Actually, however, this is far from being the case. Even in the case of gases, the transversely scattered light is known to be imperfectly polarized, and in liquids at ordinary temperatures this imperfectness of polarization of the scattered light is found to be much more strikingly evident. Taking this into account, we may, in considering the case of liquid mixtures, divide the total observed light-scattering in a direction transverse to the primary beam into three parts, which are assumed to be superposed on each other. A part Ω_1 arises from density fluctuations. A part Ω_2 arises from the concentration fluctuations. Both of these consist of polarized light, and their magnitudes are given by the thermodynamic theory already considered. Another part arises from the varying orientations of the anisotropic molecules, and this consists in great measure of unpolarized light. Denoting by r the ratio of intensity of the weak to the strong component of

polarization in the transversely scattered light, we may write

$$r = \frac{2\Omega_4}{\Omega_1 + \Omega_2 + \Omega_3 + 2\Omega_4}, \quad \dots \quad (15)$$

where $\Omega_3 + 4\Omega_4$ is the total intensity of the orientation-scattering of which a part Ω_3 consists of plane polarized light and the remaining portion, $4\Omega_4$, consists of unpolarized light, and is therefore equally divided between the two perpendicular directions of vibration. For all practical purposes Ω_3^* is negligible, and it remains to determine the magnitude of Ω_4 .

If we assume that the molecules in a liquid have their *orientations* entirely at random (though their *positions* are *not*), it is readily seen that the unpolarized part of the orientation-scattering would be simply proportional to the number of molecules n_1 and n_2 of each kind present in unit volume, and we may write

$$\Omega_4 = n_1\chi_1 + n_2\chi_2, \quad \dots \quad (16)$$

where χ_1, χ_2 are constants characteristic of each kind of molecule. The magnitude of χ_1 and χ_2 may be determined from (15) and (16) when the values of r corresponding to the case in which the liquid contains only one component or the other are known, and the values of r and Ω_4 for any given composition of the mixture may then readily be calculated. The assumption that the orientation-scattering is simply proportional to the number of molecules per unit of volume is shown to be justified by the fact that in a number of cases it enables the value of r to be successfully predicted for a single substance in the state of liquid when the corresponding value of r for the same substance in the state of vapour is known.

It is evident from (15) that when Ω_1 or Ω_2 is very large, r will be very small. In other words, when either the density scattering or the concentration scattering is very large, the transversely scattered light is almost completely polarized. The latter condition arises when the observations are made in the immediate vicinity of the critical solution temperature. The former condition arises at the plait-point temperature of the mixture, *i.e.* at a temperature which

* In the case of gases obeying Boyle's law, only 1/13 of the orientation-scattering consists of polarized light, as has been shown by Born. In the case of liquids under ordinary conditions, it is probably much smaller on account of the partial correlation of phase of the effects of contiguous molecules.

corresponds to the ordinary critical state for a simple fluid. In either of these cases, the orientation-scattering is a negligible part of the whole observed scattering.

5. Comparison of Theory and Experiment.

The theoretical results deduced above agree in their general features with experiment. The scattering of light by mixtures of phenol and water of varying concentrations has been studied in the authors' laboratory by Mr. V. S. Tamma for a range of 30° C. above its critical solution temperature (68° C.). The scattering is exceedingly large in the immediate neighbourhood of the critical solution point, and as the temperature is raised its intensity diminishes, but over the whole range the scattering remains much higher than that of the pure liquids taken together or separately. As is indicated by theory, the polarization of the light scattered in the mixture is far more complete than in pure phenol, which shows a large admixture of unpolarized light. Very near the critical solution temperature, the polarization is practically complete. But as the temperature is raised, it becomes less and less perfect.

Experiments have also been made on mixtures of ethyl alcohol and water. As the percentage of alcohol is increased, the scattering increases to a maximum, then comes down to a minimum and again increases. The extra scattering is largest for a mixture containing about 20 per cent. of alcohol. The case of this mixture is particularly complicated, inasmuch as both its compressibility and refractivity are anomalous. At 20° C., the compressibility is a minimum when the percentage by weight of alcohol is nearly 20. The refractivity of the mixture increases as the alcohol-content is increased, and reaches a maximum when there is about 80 per cent. by weight of alcohol, after which it again diminishes.

The following table gives the density-scattering calculated for different compositions in terms of that of water as a unit.

Percentage of alcohol by weight.	Compressibility at 20° × 10 ⁶ .	Refractive index at 20° C.	Density scattering.
0	49	1.3375	1.00
10	42	1.3436	0.94
20	40	1.3500	0.94
40	47	1.3600	1.20
60	62.5	1.3670	1.68
80	81	1.3693	2.19
100	100	1.3674	2.72

To calculate the concentration-scattering, we require to know the partial vapour-pressures of the components, and curiously enough, the necessary data do not seem to exist for alcohol-water mixtures. Anyhow, the concentration-scattering would vanish at about 80 per cent. by weight of alcohol, since at that point there is no change of refractivity with concentration, and would be very small over the range 60 to 100 per cent. Since the refractivity of alcohol is not very different from that of water, the effect would not be large at any stage. This agrees with the observed facts.

Measurements of the intensity and polarization of the scattered light in binary mixtures of carbon disulphide and ether, and of benzene and normal hexane have been published by W. H. Martin*. By the use of relation (15), we can calculate the orientation-scattering. Partial vapour-pressure data for the first mixture are available†, and from (14) the concentration-scattering can be calculated. But owing to lack of compressibility data, we cannot calculate the density-scattering. Since, however, this forms only a small fraction of the total scattering in the present case, an error in its estimate would not be of much consequence.

In the attached graph are shown, A the concentration-scattering, B the unpolarized scattering, and C the sum of these two for different concentrations. The values of the total experimental scattering are also plotted in curve D. It will be seen that the curve of orientation-scattering is nearly a straight line, showing, in agreement with (16), that it is proportional to the number of the two kinds of molecules per unit volume. The concentration-scattering was calculated by using (14).

Now

$$\frac{\partial \log p_2}{\partial k} = \frac{1}{p_2} \frac{\partial p_2}{\partial k} = - \frac{x^2}{p_2} \frac{\partial p_2}{\partial x},$$

where x is the mass of the first component (in this case CS_2) in unit mass of the mixture. The values of $\frac{\partial p_2}{\partial x}$ were got from the partial vapour-pressure curve of ether. $\frac{\partial \epsilon}{\partial x}$ was calculated from the formula for the refractive index of mixtures

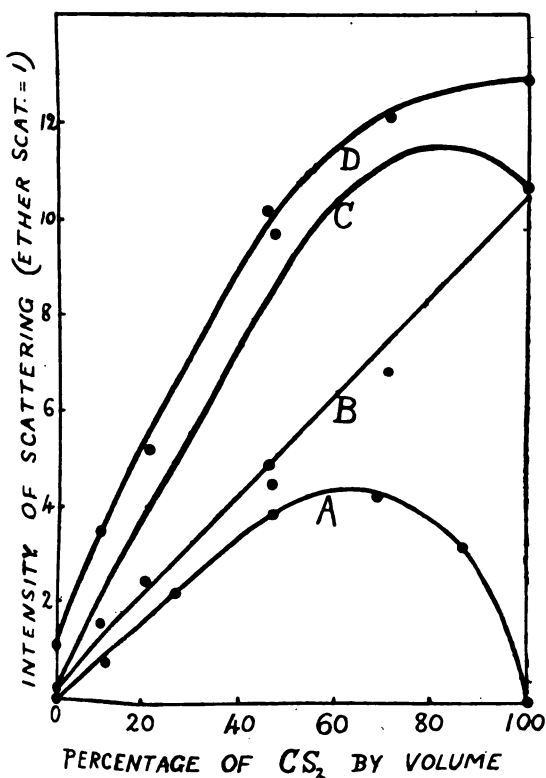
$$\frac{\epsilon - 1}{(\epsilon + 2)\rho} = \frac{\epsilon_1 - 1}{(\epsilon_1 + 2)\rho_1} x + \frac{\epsilon_2 - 1}{(\epsilon_2 + 2)\rho_2} (1 - x),$$

* Journal of Physical Chemistry, Jan. 1922.

† Guglielmo, *Acc. dei Lincei* (5) 1, i. pp. 242 & 294 (1892).

where ϵ_1 , ρ_1 , and ϵ_2 , ρ_2 refer to the two components of the mixture.

It will be noticed that the curve C closely follows the experimental intensity-curve. The difference, no doubt, represents the density-scattering, which, however, cannot be calculated theoretically (except separately for the two pure liquids) as the compressibility of the mixture is not known.



For pure ether and pure CS₂ the density-scatterings are 0.85 and 2.80, so that if these are added to the orientation-scatterings, the total scattering fits into Martin's experimental curves. To make an adequate test of the theory, we require to know both the compressibilities and the partial vapour-pressures of pairs of liquids. Data regarding partial

224 *Molecular Scattering of Light in Liquid Mixtures.*

vapour-pressures are available for a number of pairs of liquids, and the measurement of compressibilities of mixtures is being undertaken in this laboratory in order to make a complete test of the theory of light-scattering in mixtures.

Summary and Conclusion.

In this paper, the approximate investigation of the scattering of light in liquid mixtures given by Einstein is revised and a perfectly rigorous formula is developed, in which account is taken of the compressibility of the mixture. It is shown that the thermodynamical investigation leads to the result that the light-scattering arises in two distinct ways: (1) due to spontaneous local fluctuations in the composition of the mixture, and (2) due to local fluctuations of its density. Einstein's approximate investigation ignores the second effect, which becomes very important when the observations are made at temperatures not close to the critical solution point or in the case of liquids which are completely miscible at ordinary temperatures.

(a) The scattering power is expressed in terms of the compressibility of the mixture, the variations of its refractive index, and the partial vapour-pressures of its constituents with the composition.

(b) A discussion is given of the effects of molecular anisotropy which gives rise to an additional "orientation-scattering." It is shown that the polarization of the transversely scattered light is imperfect as the result of molecular anisotropy, but it is considerably less so in the mixture than in the pure liquids, and, further, it becomes more and more perfect as the critical solution temperature is approached.

(c) A comparison of the results with the available experimental data shows a general agreement.

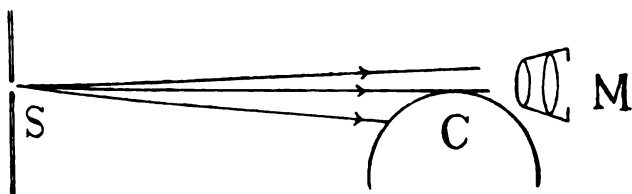
(d) Very similar methods may also be applied in the case of solutions of solids in liquids, and in the case of ternary mixtures.

Calcutta,
27th July, 1922.

XVIII. *A Qualitative Study of Inflected Waves.*By R. N. GHOSH, *M.Sc.**

IN a recent paper† the author has shown that Airy's theory of inflected wave-fronts and the supernumerary "bows" can be illustrated by ripples. The present note describes a simple optical experiment which qualitatively demonstrates the existence of inflected and cusped wave-fronts.

Fig. 1.



S is the slit which is the source (a Nernst single-filament lamp works well) from which light diverges and falls upon a silvered cylinder of glass C; M is a short-focus microscope objective ($\frac{3}{4}$ in. focal length) so placed that its focal plane is well in advance of the edge of the cylinder grazed by the incident rays. The rays after reflexion at the surface of the cylinder form a virtual caustic within the cylinder, that is the caustic becomes the virtual source of light. Hence as the rays pass through the objective M, they converge or diverge according as they lie away from or within the focal plane of M. After passage through the objective a part of the wave is converging while another is diverging, that is, we have an inflected wave-front just behind the objective. As the inflected wave travels onward, the curvature of the diverging part goes on increasing, while the other half comes to focus first and then diverges, thus folding upon the former half, and giving rise to cusped wave-fronts in the region far behind the objective M. The folding of one part over the other gives rise to interference phenomena. The principal maximum lies in the direction of the cusp where the illumination is maximum. Then we have a series of maxima and

* Communicated by the Author.

† Phil. Mag. vol. xxxv. p. 79 (1918).

‡ Proc. of Indian Assoc. vol. vi. parts iii. & iv. p. 155.

minima of decreasing width and intensity, exactly of the same type as we get in the case of an emerging wave in the rain-drop. In fact, the intensity at any point is given by Airy's integral

$$I = 4 \left[\int_0^{\infty} \cos \frac{\pi}{2} (\omega^2 - m\omega) d\omega \right]^2,$$

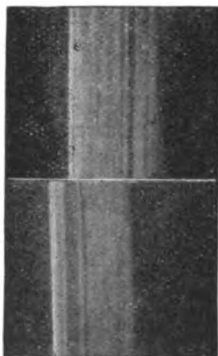
where ω and m have their usual meanings.

The existence of the inflected wave-front can be easily observed by moving a thin vertical wire (3 mm. diameter) along the wave-front just behind the microscope objective M, and observing the shadow in the region where the cusped wave-fronts are formed. As the wire is moved along the wave-front the shadow first approaches the principal maximum, and retraces its path after reaching the place of maximum illumination.

Since the shadow is in the direction of the wave normal, hence as the wire approaches the point of inflexion of the wave, the shadow moves towards the normal at the point of inflexion

Fig. 2.

Fig. 3.



(which is the direction of the principal maximum), and actually coincides with it at this point; as the wire crosses the point of inflexion the shadow moves away from the normal at the point of inflexion. This is also clear from the formation of the cusped wave-fronts, where one part of the wave on one side of the point of inflexion is folded over the other part. Hence as the wire is moved along the wave, the shadow moves along one part of the cusp, reaches it, and retraces its path along the second part of the cusped wave-front. Fig. 2 shows the shadow before its arrival at the principal maximum,

fig. 3 the same when it has retraced its path after crossing the principal maximum. It will be observed that in fig. 3 the shadow is very faint and broad, the reason being the decrease in the intensity owing to the continued divergence of the part through which the wire passes; while in the other part, it will be remembered, the wave comes to focus first and then diverges, with the result that the illumination in the latter part is much greater than in the other. In figs. 1 and 2 a few diffraction bands are observed to lie on both the sides of the shadow; these diffraction bands are the well-known Fresnel class ones.

The motion of the wire along the wave-front is always accompanied by a disturbance in the interference pattern. (1) The diffraction effects of Fresnel class are always present, but they are almost negligible when the interferences are observed at high magnification. (2) As the wire moves along, the fringe system practically disappears from the region covered by the shadow, because one part of the wave is cut off, and no interference takes place between the two parts over that region.

Some very interesting effects are observed when the wire is just on the point of inflexion of the wave. In order to observe this, care must be taken to get rid of diffraction effects due to the wire by observing the phenomena at a distance of at least 2 metres. The interposition of the wire at the point of inflexion is accompanied by (1) an increase in the number of the fringes, (2) and a diminution in their intensity, (3) and a shift of the principal maximum. In this position of the wire the shadow is not observed, but the principal maximum is replaced by a large number of faint interference fringes, which increase in their number with increasing width of the wire, but greatly diminish in their intensity. The widths of the other maxima are slightly altered. The effect of the wire upon the fringe system diminishes with their order.

Neglecting diffraction effects due to the wire, the intensity at any point can be easily calculated when a thin wire is interposed at the point of inflexion of the wave.

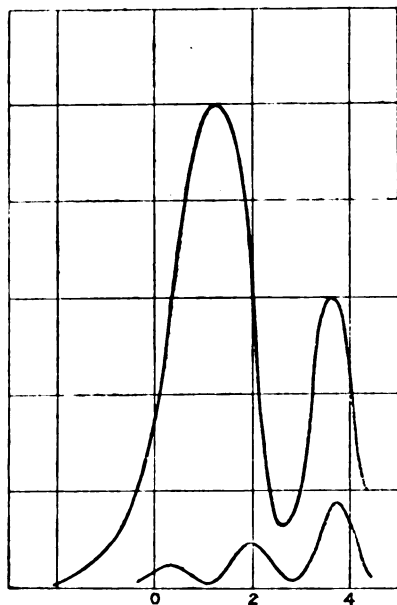
The intensity is then given by

$$I = 4 \left[\int_0^{\infty} \cos \frac{\pi}{2} (\omega^3 - m\omega) d\omega - \int_0^c \cos \frac{\pi}{2} (\omega^3 - m\omega) d\omega \right]^2, \quad (2)$$

where c is the part of the wave cut off by the wire.

In fig. 4 the upper graph represents the intensity when no wire is interposed, while the lower curve represents the intensity when a portion of the inflected wave is cut off at the point of inflexion. The experimental observation is

Fig. 4.



found to agree with the facts brought out by the curve. The increase in the number of fringes, and the diminution of the intensity, and the shift of the principal maximum are clearly shown by the curve. On a future occasion the author hopes to compare the intensities of the interference pattern before and after the interposition of the wire.

The experiments described herein were carried out in the Laboratory of the Muir Central College, Allahabad, and the author begs to record his thanks to the Physics Department, and specially to Principal J. J. Durack for placing the facilities of the laboratory at his disposal and his interest in the work.

Muir Central College,
Allahabad, India.

XIX. *Some Experiments on the Impact of Hydraulic Jets.*
By Professor A. H. GIBSON, D.Sc., and F. HEYWOOD, B.Sc.*

(1) **A**S is well known, the pressure inside the impact orifice of a Pitot tube as commonly used is very closely equivalent to that corresponding to the head of the stream impinging on the orifice. The Pitot tube is, however, almost invariably used to give the velocity at one of a series of points either in an open stream, a jet, or in fluid confined in a pipe, and the area of the orifice is always small compared with that of the stream.

No experiments would appear hitherto to have been carried out to determine what is the maximum size of a Pitot orifice which will correctly register the velocity of a given free jet. Many observers have noted that a free horizontal jet, impinging upon an orifice of its own size in the side of a vessel, is capable of maintaining in that vessel a head of water sensibly equal to the head under which the jet is discharging, which indicates that the area of a Pitot orifice may be at least equal to that of the jet to be measured, but no data are available on the effect of impact on orifices of larger area.

A consideration of the pressures involved in the course of the impact of a free jet on a hemispherical cup would tend to the conclusion that the same pressure head $\left(\frac{v^2}{2g}\right)$ as is recorded in impact on a small orifice, should be attained with an orifice of area considerably greater than that of the jet. For if the cup is of area A and the jet of area a , and if the jet is deflected through 180° on impact, the force exerted on the cup is $\frac{2wav^2}{g}$ lb., and the corresponding pressure per unit of its projected area is $\frac{2wav^2}{Ag}$ lb. or $\frac{2av^2}{Ag}$ ft. of water.

So long as A is less than $4a$, this expression is greater than $\frac{v^2}{2g}$, which indicates that the cup is too small to allow of the jet being deflected through 180° . The least size of cup which would theoretically allow the ideal pressure of $\frac{v^2}{2g}$ to be attained with full deviation of the jet, is given by $A=4a$,

* Communicated by the Authors.

and this should therefore be the least size of cup from which the full force of impact may be obtained. With a cup of larger area, the mean pressure intensity would be correspondingly less.

If, then, the phenomena of impact on an open-ended tube full of water is at all analogous to that on a hemispherical cup, it may be expected that so long as the area of this tube is less than about 4 times the area of the jet, the pressure attained in it will be sensibly independent of the area, and approximately equivalent to $\frac{v^2}{2g}$.

(2) No experimental data have hitherto been available as to the limiting area of a hemispherical cup capable of registering the full force of impact, or as to the relationship, if any, between this area and that of the maximum area of an open-ended tube capable of registering the full pressure head of the impinging jet, and the experiments to be described have been carried out in the Whitworth Engineering Laboratories of the University of Manchester with a view of investigating both points.

(3) *Experiments on impact on hemispherical cups.*

The experiments to determine the ratio between the force of impact and the size of cup, were carried out on a series of eleven hemispherical cups having diameters ranging from $\frac{1}{4}$ in. to 1 in. and with jet velocities ranging from 12 f.s. to 60 f.s. These were constructed by pressing hardened steel balls into copper or lead blocks each of which was afterwards machined so as to give a thin sharp-edged cup. This cup was mounted on a beam carefully balanced on knife-edges, and the force of impact of a jet from a parallel bell-mouth orifice vertically below the centre of the cup was measured by being directly balanced by dead weights applied to the beam.

The area and velocity of impact of the jet were obtained from measurements of the diameter of the orifice, the volume discharged, and the difference in level of the jet and the cup.

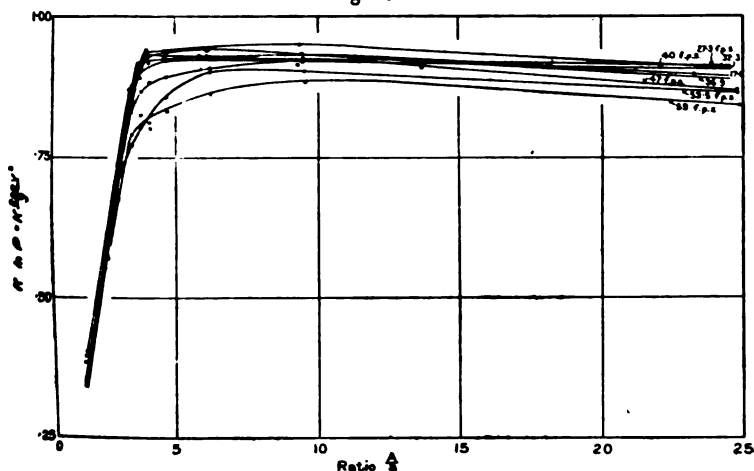
The actual force of impact is always less than the theoretical value $\frac{2war^2}{g}$ lb., partly because the angle of deviation is never the full 180° . Furthermore if the cup is of large diameter, surface friction reduces the velocity of discharge appreciably, while if of small diameter there is

some interference between the incoming and outgoing jets, and the mean angle of deviation becomes considerably less than 180° . Writing the force of impact as

$$P = k \times \frac{2war^2}{g} \text{ lb.,}$$

fig. 1 shows the relationship between the value of k and the ratio $A : a$, of the areas of cup and of jet.

Fig. 1.



From this it appears that there is a critical value of A/a , which, for all velocities, lies between 3.6 and 4.0. For smaller values of the ratio the value of k falls off rapidly according to a linear law. As A/a is increased beyond this value, k increases slightly to a maximum, afterwards diminishing, the increase being greater at high than at low velocities. For velocities up to 30 f.s. the maximum value of k is, on the average, only 1 per cent. higher than that obtained when $A/a = 4$. With higher velocities the value of A/a for maximum efficiency increases with the velocity.

Owing to the flatness of the efficiency curve in the neighbourhood of the maximum point, this point is not well defined, but its value for the jet in question may be taken for all practical purposes as follows :—

Velocity of jet f.s.	20	30	40	50	60
A/a for max. efficiency	8.0	9.0	9.9	10.7	11.5

(4) *Dimensional effect.*

Since viscosity has a comparatively small effect on the phenomena, the principle of dynamic similarity indicates that corresponding efficiencies, and corresponding maximum points, will be attained with larger jets at velocities which are greater than those given above in the ratio of the square roots of corresponding linear dimensions. Thus with a jet 3.25 in. in diameter (sixteen times that of the jet in question) a velocity of 160 ft. per second, equivalent to a head of 400 feet, would correspond to a velocity of 40 f.s. in the small jet, and for this jet diameter and this velocity a ratio $A/a = 9.9$ should give maximum efficiency.

Although there are some important differences, the hemispherical cup is to a certain extent analogous to the bucket of a Pelton Wheel, and it is of interest to note that this ratio of bucket to jet area is of the same order as has been found in practice to give best results in the case of the Pelton Wheel.

The principle of dynamic similarity also indicates that since the best ratio of A/a with a given jet increases with the jet velocity, so the best ratio with a given jet velocity should diminish as the size of jet increases. Thus utilizing the foregoing results it appears that whereas at 180 f.s. a 1.8 inch jet should have a bucket ratio of 11.5, a 7.2 inch jet at the same velocity would only require a ratio of 9.0, a result which is in general agreement with Pelton Wheel experience.

(5) *Experiments on impact tubes.*

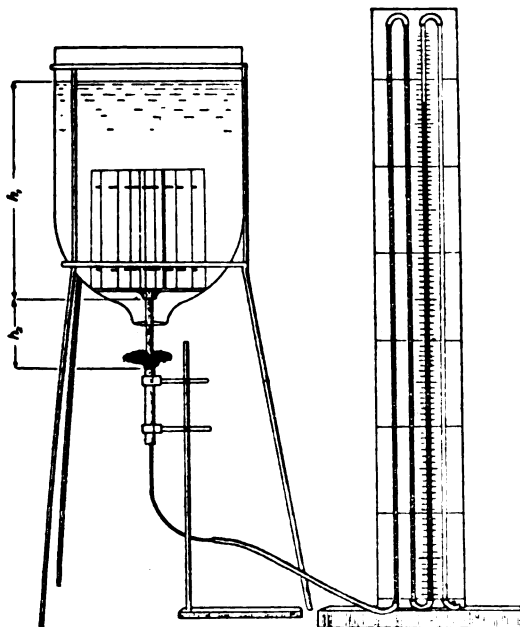
The experiments on the open ended tube consisted in allowing a vertical jet of water from an orifice in the base of a vessel to impinge on an impact tube whose height could be adjusted. A series of orifices were used, these being Borda mouthpieces of diameters 0.3, 0.4, 0.5, 0.575, and 0.7 inch, and a bell-mouthed parallel orifice of 0.5 inch diam. In conjunction with these orifices, impact tubes of the following diameters were used :—0.29, 0.37, 0.42, 0.58, 0.72, 0.84, 0.88, 1.06, and 1.5 inches.

Two series of experiments were carried out, the first with turbulent jets obtained by allowing the Borda mouthpieces to run full, and the second with steady or non-turbulent jets from the convergent mouthpiece.

In each case the impact tube was several diameters in length, was thin-walled, and parallel over its whole length. Its lower end was connected to a water gauge by which the pressure heads were recorded.

The general arrangement is shown in fig. 2. By adjusting either the head above the orifice or the distance of the impact tube from the orifice, the diameter of the jet may readily be adjusted within small limits.

Fig. 2.



Thus if h_1 (fig. 2) denotes the head of water in the containing vessel above the bottom of the orifice,

- „ h_2 denotes the distance from the orifice to top of Pitot tube,
- „ a_1 denotes the cross-sectional area of the orifice,
- „ a_2 denotes the area of the jet at level of Pitot tube,
- „ A denotes the area of Pitot tube,
- „ C_v denotes the coefficient of discharge for the orifice ;

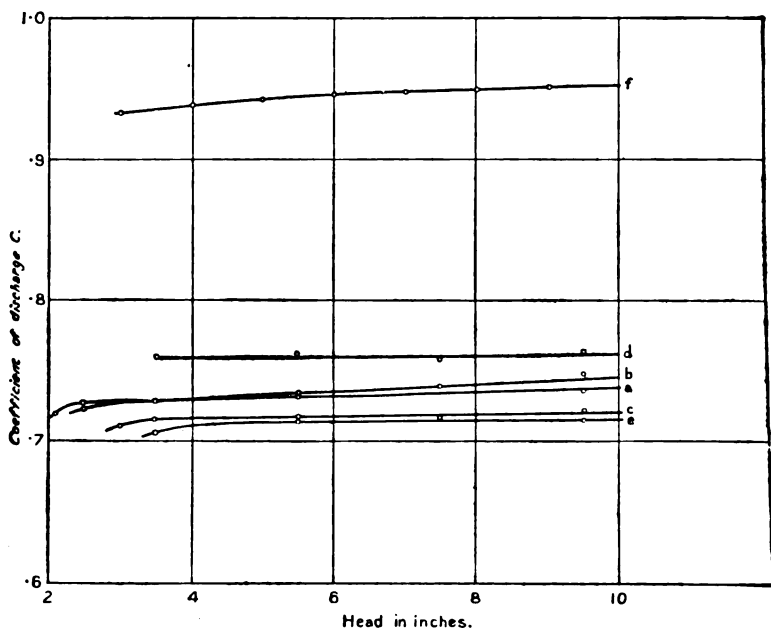
then

$$a_2 = \frac{C_v a_1 \sqrt{h_1}}{\sqrt{h_2 + C_v^2 h_1}}.$$

The values of C_v for the different orifices were carefully determined, and are shown by the curves of fig. 3.

With the turbulent jets, the recorded pressure is very unsteady, and to obtain consistent readings of the manometer it was necessary to damp out the oscillations by using a long connecting tube of small bore.

Fig. 3.



- | | |
|------------------------------|--------------------------------|
| a. 0.3 in. Borda Mouthpiece. | d. 0.575 in. Borda Mouthpiece. |
| b. 0.4 in. " " | e. 0.7 in. " " |
| c. 0.5 in. " " | f. 0.5 in. Bell Mouth Orifice. |

Expressing the pressure head as $k \frac{v^2}{2g}$, the values of k for the turbulent jets are shown in fig. 4, and for the steady jets in fig. 5. From these curves it appears that so long as the ratio A/a is less than about 3.9 for the steady jets and from 3.4 to 3.7 for the turbulent jets, the value of k is sensibly constant and approximately equal to unity. This is a critical value of the ratio and is practically identical

Fig. 4.

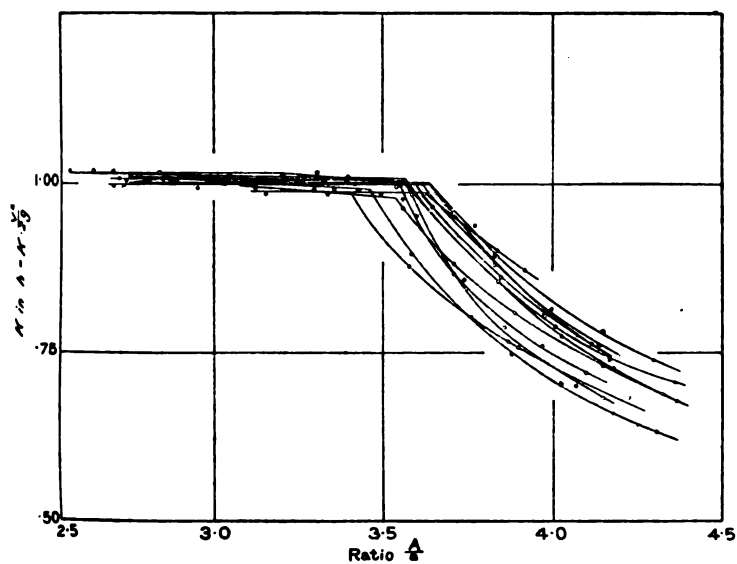
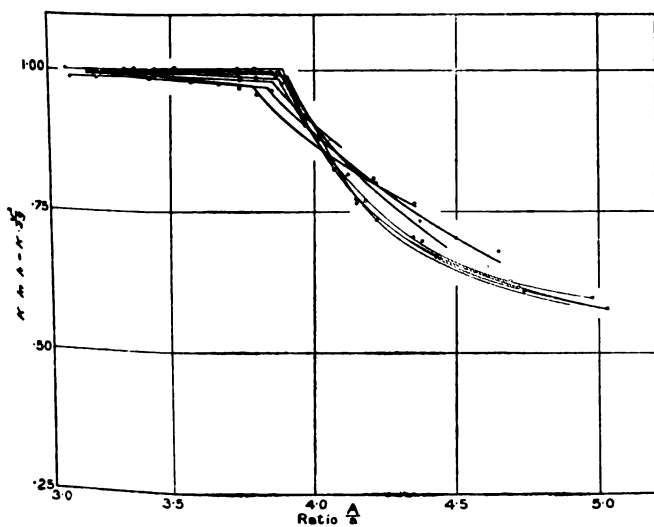
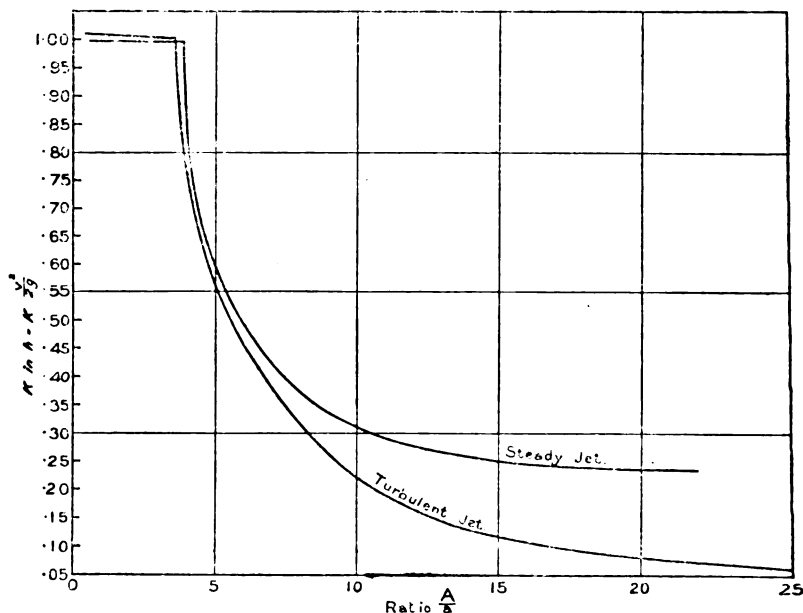


Fig. 5.



with the critical ratio found in the case of impact on a hemispherical cup. As A/a is increased beyond this point, k falls rapidly. Its values are shown in the curves of fig. 6.

Fig. 6.



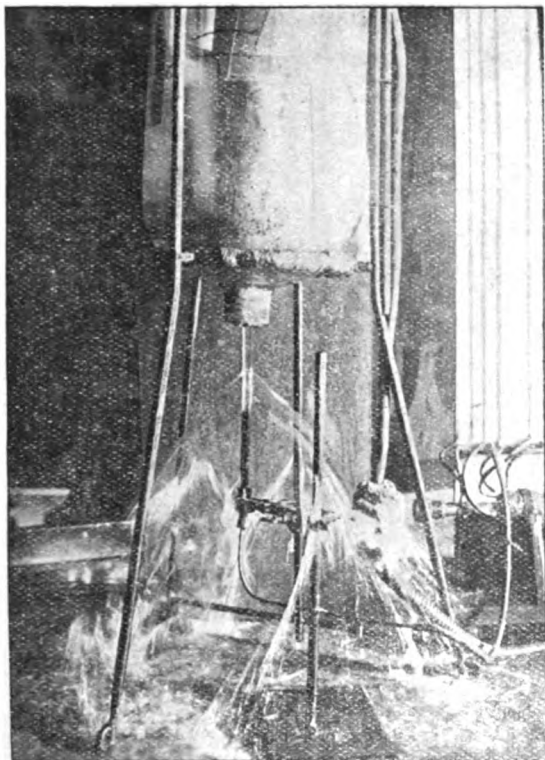
(6) The exact value of the critical ratio is very easily determined in any series of experiments. For values of the ratio smaller than and up to the critical, the water escaping around the periphery of the impact tube takes the form of a continuous clear glassy film, forming a conical surface (fig. 7) whose conical angle diminishes as A/a is increased until it attains a minimum value of 20° for a steady jet and 40° for a turbulent jet*.

The attainment of the critical area-ratio is marked by the breakdown of the film into a series of isolated drops (fig. 8), accompanied by much splashing, while whether with a steady or turbulent jet the pressure in the impact tube becomes very unsteady.

* With the vertex of the cone downwards.

(7) With the object of determining the form of the boundary between the moving and dead water within the impact tube, experiments were carried out with two glass tubes initially filled with aniline dye solution. With a stream-line jet a well-defined boundary between clear and

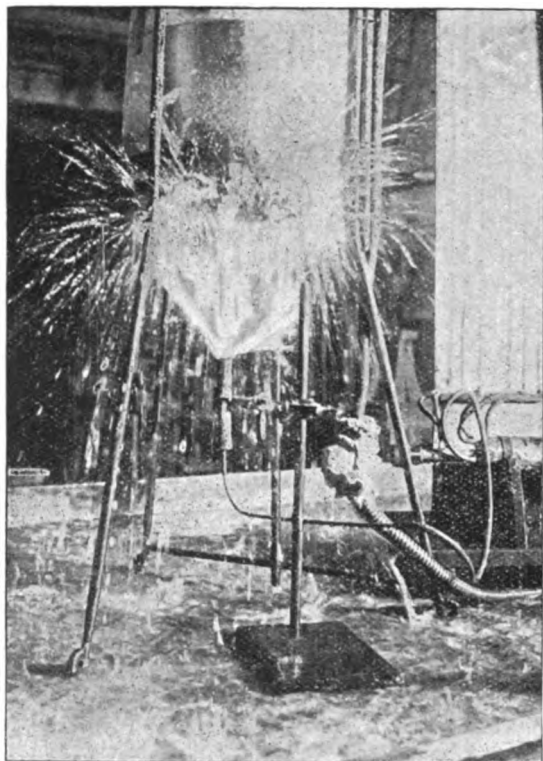
Fig. 7.



coloured water is soon established (fig. 8), and this is maintained for a considerable time. If l be the distance from the top of the tube to this boundary, and if D be the diameter of the tube and d the diameter of the jet, the value of l/D increases slightly as d increases and also as D increases. If $d/D=0.66$ its value is approximately 3.9 with a 0.4 inch

tube and 4.2 with a 0.56 inch tube, while if $d/D=0.75$ the values are respectively 4.25 and 4.45.

Fig. 8.



With a turbulent jet however, the colour in the tube is instantly dissipated.

XX. *On a Simple Derivation of the Lorentz Transformations.*

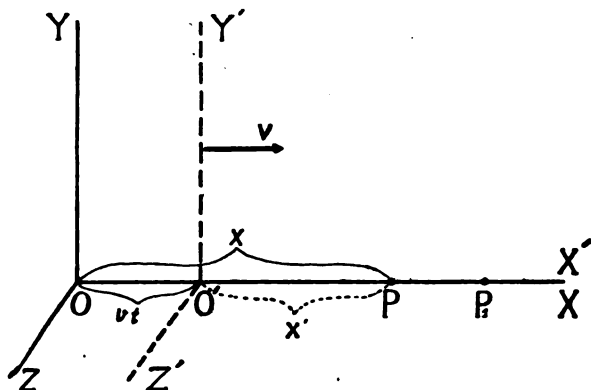
*By H. M. DADOURIAN, M.A., Ph.D., Associate Professor of Physics, Trinity College, Hartford, Conn.**

ON account of the important position which the Lorentz Transformations have come to occupy in modern physics it is desirable to make their derivation as direct and simple as possible, to give it a physical rather than a

* Communicated by the Author.

mathematical character, and to bring out clearly the postulates and assumptions which underlie each step. The following derivation of these transformations satisfies these conditions better than any other known to the writer.

Consider the x -coordinate of a point P in space referred to two systems of axes in uniform relative motion and oriented as shown in the following figure. If time is



measured in both systems from the instant the origins of the two systems are coincident, we get

$$x = vt + O'P.$$

But since space is considered as a homogeneous continuum, the value of $O'P$ obtained with the measuring instruments in the first system is proportional to the value obtained when it is measured with instruments in the second system. Therefore

$$x = vt + kx', \dots \dots \dots (1)$$

where the constant of proportionality k is a function of the velocity v .

Similarly
$$x' = v't' + k'x.$$

But two results follow immediately from the first postulate of the restricted theory of relativity:—(a) The sense of the mutual velocity is changed without any change in its magnitude when the point of view is changed from one to the other of the two systems, consequently

$$v' = -v.$$

(b) The order of points in space is not affected by a change of point of view, consequently k' and k have the same sign. On the other hand, the length of a rod placed in the first system has the same value when observed from the second

system as when the conditions are reversed, consequently k' and k have the same numerical value. Therefore

$$k' = k,$$

and
$$x' = -vt + kx. \quad (2)$$

From (1) and (2) we obtain

$$x = \frac{1}{k} (x' + vt'), \quad (3)$$

$$t = \frac{1}{k} \left(t' + \frac{1-k^2}{v} x' \right), \quad (4)$$

$$x' = \frac{1}{k} (x - vt), \quad (5)$$

$$t' = \frac{1}{k} \left(t - \frac{1-k^2}{v} x \right). \quad (6)$$

In order to determine k we apply the second postulate of the restricted theory to the following special event. A beam of light leaves the common origin of the two systems at the instant $t' = t = 0$ and reaches a point P_1 at the instant the position of P is considered. Then, since the velocity of light is the same in both systems, we have

$$x_1 = ct, \quad (7)$$

and
$$x_1' = ct_1'. \quad (8)$$

Combining (7) and (8) with (3) and (5) after introducing subscripts into the latter pair to indicate the special character of the event under consideration, we obtain

$$x_1 = \frac{1}{k} \left(1 + \frac{v}{c} \right) x_1', \quad (9)$$

and
$$x_1' = \frac{1}{k} \left(1 - \frac{v}{c} \right) x_1; \quad (10)$$

which give
$$k = \sqrt{1 - \frac{v^2}{c^2}}. \quad (11)$$

Introducing this value of k in equations (3) to (6) we obtain the famous transformations.

It may be stated parenthetically that the world-points representing the events of the arrival of the beam of light at the points P at the specified instants lie on one of the two light-lines of the xt -plane and satisfy the following conditions :

$$x_1' = \sqrt{\frac{c-v}{c+v}} x_1,$$

$$t_1' = \sqrt{\frac{c-v}{c+v}} t_1.$$

XXI. *On the Occlusion of Hydrogen in Palladium.**By* MITUO YAMADA*.

[Plate II.]

IT is a well-known fact that the metal palladium absorbs a large quantity of hydrogen gas. But the mechanism of the absorption has not yet been made clear. Some authors explain this absorption as a consequence of the formation of a compound of hydrogen and palladium, while others suppose a state of solid solution of these two elements. Hence I have made an experiment on this point by X-ray analysis, which affords a final judgment about questions of this kind.

The method applied is that of Debye-Sherrer, and the apparatus are not very different from those of Hull. A thin beam of the X ray from a Coolidge tube with a molybdenum anticathode, after passing through a filter of zirconium oxide, strikes the specimen at the centre of a cylinder, around which the photographic film is fixed together with an intensifying screen. The diameter of the cylinder is 7.3 cm. The specimens were made of a wire of palladium metal 0.5 mm. thick. A röntgenogram, which is shown in fig. 1 (Pl. II.), was first taken with a specimen free from hydrogen. Then the palladium wire was made to absorb hydrogen by electrolysis, putting it in dilute sulphuric acid as the cathode and using a platinum wire as the anode. The wire after absorbing hydrogen showed considerable dilatation. The röntgenogram of this specimen is shown in fig. 2 (Pl. II.).

Comparing these two figures, we cannot find any difference except the slight contractions of the intervals of the lines in fig. 2. Hence the arrangement of the palladium atoms is not altered by absorbing the hydrogen gas. The slight contraction of the intervals of the lines in fig. 2 corresponds to the uniform expansion of the space lattice.

If the absorption of hydrogen accompanies the formation of a compound, then the arrangement of the palladium atoms in the compound must be entirely different from that in the normal state. Hence we must expect the appearance of new lines which correspond to the compound. But we do not find any new lines in fig. 2. The difference which we observe is only slight displacements of the lines in fig. 2

* Communicated by the Author.

towards the centre. Hence the following three cases remain possible :—

(i.) The atomic arrangement of palladium atoms in the compound formed is the same as that in the normal state, differing only in their dimensions, and the lines in fig. 2 correspond to this compound.

(ii.) The compound formed is too small in quantity to reveal the lines of sufficient intensity, and the lines in fig. 2 correspond to the palladium remaining in the normal state.

(iii.) The hydrogen is absorbed in the state of solid solution.

The first possibility can be excluded, if we consider the course of the displacement of the lines by changing the percentage of the absorbed hydrogen. A röntgenogram* obtained with a specimen containing a quantity of the hydrogen less than the specimen in fig. 2 showed lines which fell just between the corresponding lines in figs. 1 and 2. If a compound is formed, the transition of the lines must be the gradual disappearance of the lines of palladium in the normal state followed by the appearance of the lines of the compound accompanying this, and not a continuous displacement of the position of lines.

The second case cannot also be possible. In this case the appearance of no new lines can be understood, but we must explain the slight displacement of the lines by the change of the space lattice of the palladium crystal in the specimen. We see from fig. 2 that this change of the lattice is a uniform expansion. This strain necessitates an enormous tension, uniform over all directions. Whatever the volume and form of the compound formed may be, the internal stress in the palladium crystals caused by the production of the compound must be of a very heterogeneous nature, conditioned by the form of the grain boundaries. Hence in this second case the lines must appear as diffused lines, and not as sharp lines displaced, and this possibility is excluded.

On the other hand, if we assume the third case, the results of the experiment can be explained perfectly. Vegard† showed that the solid solution does not reveal any new lines, but a small displacement of lines. Therefore we can without any doubt conclude that the hydrogen is absorbed in the palladium as a solid solution of these two elements.

* Fig. 3 (Pl. II.) shows a few lines of these three röntgenograms. The lines on the middle line are those of fig. 1, the lines on the upper side those of fig. 2, and those at the lower side are the lines of this third röntgenogram.

† L. Vegard, *Zeitschr. für Phys.* v. p. 17 (1921).

The specimen in fig. 2 absorbed nearly 660 times of its volume of the hydrogen gas at room temperature and normal pressure. The molecular percentage of the absorbed quantity was 29 per cent. The quantity of hydrogen was determined by expelling it by heating, after the röntgenogram was obtained. The expansion of the lattice determined by the displacement of the lines was 2·8 per cent, while the expansion of the specimen obtained by the direct measurement of its diameter was 2·9 per cent. This coincidence shows that the expansion of the specimen is due solely to the expansion of the lattice caused by the absorbed hydrogen.

My cordial thanks are due to Prof. K. Honda, under whose kind directions this investigation was carried out.

Iron and Steel Research Institute,
Tohoku Imperial University, Sendai, Japan.

XXII. *On the Nature and Amount of the Gravitational Deflexion of Light.* By Sir JOSEPH LARMOR, F.R.S.*

1. **T**HE deviation of the rays of light in a gravitational field has proved to be the most searching criterion hitherto available, to discriminate between various ways of forcing gravitation to come within the crucial electrodynamic principle, which assures that velocity of translatory convection of a material system must remain latent in all local physical tests.

The observations at the solar eclipse of 1919 have confirmed on the whole the prediction of the amount of the effect which had been assigned on the basis of the Einstein formulations. But the object of this note is to support a suggestion that the implications of that intricate and beautiful analytical theory have not perhaps even yet been sufficiently explored,—in fact to submit for critical examination an estimate of the deviation of light that is reduced to one half. Though the general theory has been worked over many times in great analytical detail during the last six years, it does not appear that the order of ideas here developed has been closely dealt with.

The guiding considerations are contained in §§ 2, 3; these were originally drafted in anticipation of the recent Solar eclipse, of Sept. 21, which it was hoped would decide, at any rate practically, the questions there submitted. The other sections, some in part memoranda for future constructive

* Communicated by the Author.

application *, have grown up around them from a desire to probe, on all sides, an argument which seems to be in conflict with main dogmatic postulates of the recent relativity theory. Thus on the present view gravitation would not be absorbed into the spatial frame of reference: so the free path of a particle remains a dynamical orbit in the usual sense, and is not merely a straightest path, in the fourfold extension determined by electrodynamics but modified slightly by gravitation. The "principle of equivalence" between a field of gravitation and a field of acceleration would thus seem definitely to fail: indeed its only application was to connect radiation with gravitation.

The argument would therefore affect fundamentally what was the original primary motive of the relativity theory, the effort to dispense with frames of reference other than those directly afforded by the local part of the material system itself. Any modified formulation such as is here submitted must of course be based on the mathematical work of Einstein, and would not in any case impair the value of his resourceful algebraic synthesis, or the general analytical trend of his mode of adapting gravitation into an electrodynamic frame. The intricacies in this subject are however not in mathematical theory, which however complex is yet straightforward; and they are indeed of long standing, going back to the critiques of Leibniz on the *Principia*; in modern form they are concerned with physical interpretations of the same scheme of equations within different analytic frames, including the mode of adaptation from fourfold frames into the practical Newtonian world of astronomy.

This procedure of practical adaptation into Newtonian space and time, even if adequately coherent within its limited range, which fortunately includes the actual world, may be judged timid and unenterprising. The more robust alternative appears to be to postulate that the world of so-called classical physical science is an illusion, an imperfect picture of a reality depending symbolically on a field of fourfold quasi-geometrical algebra, of a presumed cosmos deep below the sensual sources of our concrete physical knowledge, of

* The present paper was completed as it stands (with additional matter) in the middle of last October, except the final part which was drawn up early in November in reply to criticism.

The writer is aware that the weight of expert authority must be against him, and therefore that the chances are not in favour of the correctness of his conclusions: but he still thinks that the subject requires rather urgently to be cleared up, and that early publication of his argument may serve as a first step in that direction.

Compare the destructive criticism of the postulate that orbits are mutual, yet also geodesic curves by J. Le Roux, *Comptes Rendus*, Nov. 6, p. 809, and Dec. 4, p. 1135.

which we may obtain shadowy glimpses, but which is as yet quite beyond any direct grasp or intuition. Atoms of matter would almost disappear as the permanent sources of phenomena: there would be only "world-filaments," in the fourfold, of nearly uniform density, and reality would be merely the pattern of their intersections. The rigour of this procrustean geometric scheme will have to be relaxed, if it is ever to take the place of the flexible formulations of historical physical science.

Yet this fourfold presentation may not be evaded, even though it represents a world entirely foreign to our practical knowledge. For the principle of what may be called the indifference of space, extended after Minkowski and Einstein into the test of isotropic fourfold space-time invariance of the scheme of equations, is imperative. It may be said to take its origin nearly a century ago with Green and MacCullagh, in their general doctrine of isotropic elastic media, real or ideal, developed on Lagrangean principles: in their theoretical constructions the form of the Action function was determined by its local differential invariance, as expressed by the test that the orientation of the local Cartesian spatial lattice-frame of reference could have no influence on its character. The transfer of this principle of spatial invariance into the fourfold extension is the determining criterion in the electrodynamic analysis: and it may perhaps be held to be only accidental that the relevant group of equivalent fourfold frames involves a merging into insignificance of what in the Newtonian world is prominent as local translatory velocity. Where then does this foundation principle of the quasi-geometrical fourfold and its local directional indifference take its origin? If we postulate that the Action is wholly distributed as an Action-density, to be integrated over space and time, that is virtually if we assume that all activity is in a medium of which the particles are merely passive determining singular points, or more precisely, local interfaces of discontinuity which contribute nothing to the Action directly, then the problem of choosing the form of the Action so as to satisfy this condition of invariance becomes a possible and even feasible one, without further limitation. The discussion resolves itself mainly into fixing the nature and extent of the group of transformations for which the invariance subsists. The multiple product $dx dy dz dt$, expressing the differential element of extension involved in the Action integral, must be separately invariant except as regards a factor depending on position. This is obviously secured if δx , δy , δz , δt belong to local coordinates in a fourfold flat extension. But if time were merely an extra dimension of space, the spatial characteristic of locality in

the fourfold would prevent the local time from ranging without limit within a material system limited in space. This is avoided by making time an imaginary instead of a real dimension in the fourfold; then the attribute of locality persists as regards positions, which can remain adjacent, not as regards time. To establish any quasi-spatial connexion at all between space and time involves an absolute constant c , of the nature of a velocity when interpreted into Newtonian space: the case of Newtonian space and separate time in which alone an idea of velocity is effective appears as the limit as c tends to an infinite value. Thus the fourfold is the natural and only possible further generalization, after the manner of Green, of the principle of minimal Action extended throughout a medium, which is the final unification of Newtonian physics. And the principle of Action maintains its ground as the ultimate unresolvable dynamical unification, as the ideal method for safe and consistent analysis of intricate physical systems.

2. *The relation of gravitation to mass.*--Any approximate analysis must on this order of ideas lead to a field of gravitational potential belonging to each piece of matter, determined say by its mass-inertia m : for the usual velocities of physical astronomy it is to sufficient approximation a radial field, of intensity μ/r for each body, where μ is some property of that piece of matter, perhaps some function of m in default of other suggestions. The equations of motion of another mass m' in this field are taken to be of type

$$m'\ddot{x} = m' \times \text{component of } \mu/r^2.$$

The implication that it is the same m' that occurs on both sides of the equation, and thus disappears from the problem of free orbits (in a specified field) by cancelling, involves the principle of Newton, experimentally tested by him and confirmed with precision by Bessel and finally within 5 parts in 10^8 by Eötvös*, that masses of whatever kinds of matter behave to a pervading gravitational field in a manner determined by the aggregates of their inertias alone, and therefore when free and started alike travel so as to remain together †.

It is a further principle of Newton's formulation in the *Principia* that gravitational attraction between two masses obeys his law of balanced mutual forces: for otherwise as time flows onward the joint motion of the bodies relative to the uniform Newtonian frame would increase without limit.

* The effects on planetary perihelia seem to depend on terms in the equations of rather less than this order of relative magnitude.

† Cf. *Principia*, *Leges Motus*, *Lex iii. cor. 6*.

But so far as we have yet gone the attraction of m_1 on m_2 is $\mu_1 m_2/r^2$, while the attraction of m_2 on m_1 is $\mu_2 m_1/r^2$: these cannot balance unless $\mu = \gamma m$, and then the mutual force is the Newtonian $\gamma m_1 m_2/r^2$. The direct evidence (apart from the principle of Action, as *infra*) settling the degree of verified validity of this formula is not terrestrial experiment, but the whole fabric of physical astronomy: the precision of that evidence is in the main far below the Eötvös standard.

In theory this principle requires some formulation purely dynamical: thus the way to get nearer to it is by a dynamical path,—in fact through the principle of minimal Action which, mainly in Hamilton's hands, became the condensed expression of the essentials of general dynamical science.

In the Minkowskian fourfold frame of reference, which is the most effective setting for abstract electrodynamics, in which time runs parallel (and entangled) with spatial coordinates, not of course completely parallel for it is not spatial, the only expression that could be appropriate for the Action A of a free moving particle is

$$A = \int \nu ds, \quad \text{where} \quad ds^2 = c^2 dt^2 - dx^2 - dy^2 - dz^2,$$

and ν depends on its mass m . The condition of invariance for change of fourfold Cartesian frame restricts A to this form. On expanding in a series, to bring it into line with the forms familiar in ordinary dynamics,

$$\begin{aligned} A &= \int \nu c dt \left(1 - \frac{1}{2} \frac{v^2}{c^2} + \dots \right), \quad \text{where } v^2 = \dot{x}^2 + \dot{y}^2 + \dot{z}^2 \\ &= \nu c t \left| - \int \left(\frac{1}{2} \frac{\nu}{c} v^2 + \dots \right) dt. \right. \end{aligned}$$

When this is interpreted into a Newtonian frame, namely x, y, z and separate t , it should approximate to the Hamiltonian free Action $\int T dt$ where $T = \frac{1}{2} m v^2$. Hence $\nu = -cm$.

If the particle m , instead of being free, moves in a field of force say of potential (energy) U per unit mass, A should approximate for ordinary velocities to $\int (T - W) dt$, where $W = mU$; for that is the form of the Action in the Newtonian frame. This requirement can be secured, with sufficient approximation, very simply, by changing from c to c' in the equation for ds in the Action $A = - \int c m ds$, where

$$c' = c \left(1 + \frac{U}{c^2} \right).$$

This result carries the suggestion that gravitation can be pressed into the Minkowskian electrodynamic fourfold, which

concentrates into intuitive form the Lorentz group of transformations of ordinary space and time, by slight local change of the velocity of light, proportional to the potential of the field at each place. This procedure would insert gravitation, or any other field of force, into the electrodynamic scheme, itself slightly modified thereby: but of course for this very reason, that it does not point to any special law of the field, it is no explanation. Partial or local frames with different values for c' would have to be coherent, that is to merge together into a single continuous universal fourfold frame, just as the local maps of the surface of the Earth have to be made to fit together into a coherent whole. It is the main problem of hypergeometry to determine the integral form for this continuum: a solution could doubtless be effected for any assigned type of field when, on account of the greatness of c , the warping of the frame from flatness is slight.

The next step in this order of tentative development would be the discussion of the Action of a system constituted of two masses, if we could assume it off-hand to be

$$A = - \int m_1 c ds_1 - \int m_2 c ds_2.$$

But this formula is as yet quite without warrant: though it is the necessary foundation of the material tensor that arises in the adjustments of the relativity formulation. When the fields of activity of two physical systems are superposed in the same region, their Actions are not to be simply added without special reason assigned, for they involve quadratic forms just as do the energies.

We have in fact to deal with a physical field of which m_1 is the nucleus, and which in its ramification from m_1 surrounds and influences m_2 , or rather influences the field of m_2 which controls m_2 as its own passive nucleus,—and *vice versa*. This involves a single compound field of joint Action-density in the fourfold, determined by m_1 and m_2 as point-poles or nuclei keying up that field, that being a specification of the masses which is sufficient for the present purpose. It is the essential characteristic of this order of ideas, as here developed, that the Action is required to be located in ultimate analysis in the field alone; thus it is expressed as a fourfold integral, which must be invariant for transformations within the group of frames which all express by means of different coordinates the same essential spatial spread. This requirement as regards form severely restricts, as has been seen, the extent of the group of frames that are permissible, as being equivalent as regards complete free interchange from one to another.

Now in the fourfold extension, everywhere to a first

approximation locally flat, the threefold spatial part has to remain compact or coherent for a wide group of transformations by continuous change, and therefore (Helmholtz, Lie) it has the Euclidean distance-relation; and the attachment to it of a fourth, though imaginary, dimension *ict*, which is such as must maintain as above invariance of differential fourfold extent, seems to involve that the fourfold also is (differentially) Euclidean. This result appears to be the source and the essential significance of the Minkowskian fourfold representation: it defines, to its utmost possible extent, the group of changes of frame with respect to which an extended distribution of Action, of density purely continuous, could possibly exhibit invariance. Radiation is invariant in the fourfold, for the Action-density of the electrodynamic field is readily shown to be so: and the experimental facts (Michelson and Morley and Miller, Rayleigh and Brace, Trouton and Noble) invite us to force material dynamics and gravitation into this group of equivalent fourfold frames, and so take them out of the different Newtonian group corresponding to c infinite, in which their sciences have formally been developed,—in preference probably to the older reverse procedure of modifying electrodynamics by shrinkage of the sources of its field so as to retain it within a Newtonian frame, which would perhaps in any extensive development be more complex and artificial. Or, from a different point of view: the invariant formulation in terms of pure algebraic quantity is the essential scheme: the element in it which on a Newtonian kinematic interpretation is the local velocity is merged, in an interpretation into the fourfold spread of space-time, with mere local orientation of the inessential Cartesian reference-lattice.

As then has recently been well-known, there is only one spatial differential invariant, necessarily of considerable analytical complexity, that is appropriate thus to serve, though with certain unusual if not anomalous features, as an Action-density in the fourfold expanse, now formulated as of unrestricted Riemann type, varying from place to place; namely the invariant of local curvature very briefly indicated in outline by Riemann himself for n -fold extension in a formal thesis in Latin, towards the last days of his short life*. The Action-density is thus determined in general type for a gravitational field, if forms of entirely unmanageable complexity are set aside, except as regards a constant

* The ideal would perhaps be a mixed invariant, entangling gravitation with the electric field, instead of an independent spatial form which satisfies experience in the main but leaves gravitation an isolated phenomenon.

multiplier which prescribes scale of magnitude of gravitation. The minimal condition, which may be described as ensuring that the Action is distributed as regards form and density at a uniform level throughout all the extension, then determines restrictions on the general Riemann type of space which may be described as the laws of structure in the gravitational fourfold. It was shown by an approximate analysis, by Einstein and more systematically by Hilbert, that the field thus reduced spatially to minimal Action, is determined by a criterion of Laplacian form, (as was almost inevitable in invariant analysis) so as to be around each mass m of the type specified by the form of ds^2 sketched empirically above (p. 248) as appropriate to gravitation: while the exact analytical solution for the field of a single isolated mass was worked out soon after by Schwarzschild and by Droste.

The Action, after thus being adjusted to minimal form throughout the free extension which is its seat, proves of course to be of very great local density in the region close around one of its determining poles or material aggregations, and thus integrates spatially, when referred to a coordinate frame attached to the pole, to a finite amount which may be described as belonging to that pole; this spatial integration aggregates the local part of the Action as a time-integral, which it is not necessary to analyze in closer detail except in a discussion of atomic structure; it constitutes a material term, in addition to the general fourfold distribution of Action which can now ignore the accumulation around the local core. If we denote this separated material part by $-\int mc^2 dt$, then when transferred to an unrestricted frame not attached to the particle, it must change to $-\int mcds$ in order to be of the necessary invariant type. The result for two mass-particles* m_1 and m_2 is

$$A = -\int m_1 c ds_1 - \int m_2 c ds_2 + \text{a fourfold integral.}$$

It so happens, very remarkably and even appropriately from our present point of view, that when there is no electric field the density of the latter continuous part, as now adjusted to minimal spatial distribution, is always and everywhere null, so that the whole of the Action is concentrated within and around the pole-structures or particles of matter. The laws of material dynamics are involved in its further minimization, as regards the positions of the particles.

If then the atoms of matter are passive pole-structures,

* In further elucidation, the cognate reduction for the local Action of electrons in motion in an electrodynamic field, in the Maxwellian frame, as effected in 'Ether and Matter' (1900) § 56, may be compared.

singularities of local beknottedness keying up strain of some kind in a surrounding and intervening active medium which is at each moment practically in internal equilibrium, through adjustment by a process analogous to elastic spatial waves, this argument shows that the Actions belonging to them are correctly to be added together, on account of this equilibrium. The only way to evade this indirect conclusion, as expressed in the formula above, would be by the possibility of a mutual, or mixed, invariant term* involving both the masses: it would appear however that any such feasible term must be based on the scalar fourfold product (ds_1, ds_2) , which is already recognized as the basis of the electrodynamic Action between two electric charges carried by the particles ‡ and so is excluded from any other interpretation.

3. *The orbital problem for two masses.*—Writing the exact Schwarzschild form for ds^2 (though the original Einstein approximation which only made the measure of time variable would be sufficient for the present purpose) as if each pole were isolated, for the reason above sketched, we have now for the two interacting particles m_1 and m_2 which originate the field,

$$A = - \int m_1 c \left\{ c^2 \left(1 - \frac{\mu_2}{r}\right) dt^2 - \left(1 - \frac{\mu_2}{r}\right)^{-1} dr^2 - r^2 d\theta_1^2 - r^2 \sin^2 \theta_1 d\phi_1^2 \right\}^{\frac{1}{2}} \\ - \int m_2 c \left\{ c^2 \left(1 - \frac{\mu_1}{r}\right) dt^2 - \left(1 - \frac{\mu_1}{r}\right)^{-1} dr^2 - r^2 d\theta_2^2 - r^2 \sin^2 \theta_2 d\phi_2^2 \right\}^{\frac{1}{2}},$$

in which r represents r_{12} ; and expanding in series so as to change into a form amenable to direct interpretation into a Newtonian frame with (x, y, z) as Euclidean space and separate t ,

$$A = \int dt \left\{ -m_1 c^2 + \frac{1}{2} \frac{c^2 m_1 \mu_2}{r} + \frac{1}{2} m_1 v_1^2 + \frac{1}{2} \frac{m_1 \mu_2}{r} \left(\frac{dr}{dt}\right)^2 + \dots \right\} \\ + \int dt \left\{ -m_2 c^2 + \frac{1}{2} \frac{c^2 m_2 \mu_1}{r} + \frac{1}{2} m_2 v_2^2 + \frac{1}{2} \frac{m_2 \mu_1}{r} \left(\frac{dr}{dt}\right)^2 + \dots \right\},$$

in which v_1, v_2 are the velocities of m_1 and m_2 in the frame;

* Any regional distribution of a gravitational momentum, such as makes the compensation in the case of the electrodynamic stress-tensor, at any rate of amount such as would affect the present argument, is wholly excluded by the slowness of the motions of matter.

† Its value is $\int e_1 e_2 (\dot{x}_1 \dot{x}_2 + \dot{y}_1 \dot{y}_2 + \dot{z}_1 \dot{z}_2 - c^2) r_{12}^{-1} dt$ where r_{12} is distance in the fourfold, when gravitation is neglected; being symmetrical with respect to both ends, it is in strong contrast to the type of the gravitational Action.

or, retaining only terms of primary importance,

$$A = \dots + \int dt \left(\frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2 + \frac{1}{2} c^2 \frac{m_1 \mu_2 + m_2 \mu_1}{r} \right).$$

As the adjusting gravitational pulses in the threefold would travel at the speed of light, it can be assumed as above that the field of each mass is completely adjusted in the space around it at each instant. The attraction, indicated by the potential term, is mutual, as the Newtonian principle requires.

But the Newtonian Action which in the threefold determines in the usual dynamics the mutual elliptic orbits of two masses is

$$A = \int (T - W) dt = \int dt \left(\frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2 + \frac{\gamma m_1 m_2}{r} + \text{const.} \right)$$

where γ is the constant of gravitation. To identify this with the form at which we have arrived it is necessary to make μ^* equal to $\gamma m/c^2$ [not the usual $2\gamma m/c^2$].

Indeed now we are in a position to appeal from the previous less approximate evidence of general physical astronomy to the closer limits afforded by the Eötvös torsion-balance applied to terrestrial centrifugal force, to fortify this result: for it is required by the latter that $\frac{1}{2}(m_1 \mu_2 + m_2 \mu_1)$ shall be proportional to m_1 up to 5 parts in 10^8 , which is almost the order of the electrodynamic convectional verifications. But the principle remains an experimental one for which theory as yet assigns no reason.

It is the very indirect way in which gravitation appears, through an arbitrary constant of integration μ within the bracket in A, that is the source of the inadequacy of a formal quasi-spatial tensor theory as regards orbital problems, if the present argument holds.

It may be of interest to observe a parallelism, in this discussion of the gravitational problem of two free bodies, with the premature effort of Helmholtz, in his great memoir (1847) on the Conservation of Energy (as reproduced in Maxwell 'Treatise,' vol. ii. § 544) to derive the interactions of two linear electric currents from the single equation of Energy alone. There also a problem of two variables demanded a wider principle leading to more than one equation, such as would be expressible as minimal Action; and it is the same liability to count a mutual term twice that is thereby avoided.

The question of the frame of reference to which the velocities in this argument are to be referred perhaps demands further attention. In the first place as to the static

* The quantities μ here, namely μ_1 and μ_2 in A, are new entities, identified only ultimately with the μ of § 2: which may be a cause of confusion.

field of an isolated mass : it is the field developed practically instantaneously, referred to a frame practically Newtonian, or Galileian as it is now often named *, which travels along with the mass but without rotation relative to its motion. Alternatively, the reference can be to any equivalent frame, that is, to one convected with uniform translatory velocity relative to the former. It will then be the square of the velocity relative to this new frame that occurs in the approximate expression for the Action ; while the potential energy, involving only r , is independent of the frame. The static fields of m_1 and m_2 thus may at first refer to different frames, in which the masses may have any velocities ; until by virtue of equivalence within each of two groups of frames we choose a common frame suitable for both moving masses, in which the analysis can be conducted. This comes to asserting that any one of the Newtonian group of frames, differing with respect to uniform translatory velocity, is suitable for expression of the Action of two, or more, masses by simple summation, in sufficient first approximation for practical cases : and the choice that remains open between the members of the group is the expression of the original Newtonian dynamical relativity.

The deviation of a ray of light in the neighbourhood of a large mass m is determined by electrodynamic principles in terms of the local form of the fourfold electrodynamic spatial datum ds^2 as dominated by that mass, which we have found to be

$$ds^2 = c^2 \left(1 - \frac{\gamma m}{c^2 r} \right) dt^2 - \left(1 - \frac{\gamma m}{c^2 r} \right)^{-1} dr^2 - r^2 d\theta^2 - r^2 \sin^2 \theta d\phi^2.$$

This is different from the form used by Einstein, and by others expounding and developing his theory, in that it involves γ instead of 2γ . The reason is that the constants in this form have been fixed by comparison with the Newtonian Action for the problem of *two* interacting bodies, in which gravitation appears not as a spatial form but as a mutual potential (energy) of their two fields, and must not be counted twice over, once for each.

* The name frames of inertia was proposed long ago by James Thomson, the only brother of Lord Kelvin, who first introduced the idea of equivalent frames of reference : see 'Inertia, Chronometry, Absolute Rotation,' Proc. Roy. Soc. Edin. 1884, or 'Collected Papers,' pp. 379-88. The paper next following, in the same year, discusses a problem whose mere statement is reminiscent of the current gravitational doctrine : given a system of particles in changing mutual configuration, to determine where possible a (moving) frame of constant configuration relative to which each of the particles is in uniform rectilinear motion. In other words, his problem is to determine in what cases the forces of a set of moving particles can be absorbed into a moving frame of reference.

Unless then there is some discrepancy lurking in this development of the dynamical method through analysis of the Action, the deviation of the rays of light should be reduced to half the usually accepted expression. For example, the summary appeal to invariance, in order to fix general forms, which is a main resource of the analytical theory, might conceivably here be misleading. But the systematic deduction from the Action principle seems to provide a security, in this regard, which is absent from a procedure by formal adaptations and adjustments. If the argument proves to be sound, the same reduction to one half would apply to the predicted displacement of periods in solar spectra. But the influence on physical astronomy, which has in fact been used to fix the constants, would remain unchanged*.

An alternative which may conceivably be proposed is to reject dynamics and its relevant Action principle altogether, as transcended by the transfer from Newtonian space and time into fourfold extension; in fact to work in Einstein's manner with formal adjustable stress-tensors possibly not amenable to that law. But then the theory seems to lose all cohesion; there would be no reason except empirical convenience, for identifying μ , which enters into the fourfold solution for the field of a point-mass merely as an arbitrary constant of integration and so completely from outside, with either value γm or $2\gamma m$, or indeed for connecting it in any way with m . If then we allow ourselves to contemplate that astronomical observation may not verify the expression, whichever be the appropriate one, for the gravitational deviation of light, what would be the inference? At the worst, that gravitation would remain, as previously, outside the electrodynamic group of inessential transformations between sets of coordinates belonging to the same one essential spatial fourfold which makes translatory convection undetectable; and so gravitation would slightly disturb that result.

For at best this beautiful and intricate formulation cannot be held to explain gravitation. To do that it would have to connect the value of γ with other universal constants of atomic structure: whereas, as it stands, γ might quite well (indeed with great increase of simplicity) be zero, when we would have a world without gravitation altogether. The theory merely explains one way by which gravitation, assumed to exist independently, can be modified so as to come under the electrodynamic principle of the insignificance of local convection.

* Its adequacy to explain the outstanding perihelion motion of Mercury has however recently been placed in doubt by a recension of the standard calculations by the astronomer E. Grossmann.

Not the least remarkable feature of the fourfold formulation, as has often been dwelt on in more complicated ways, is the mode of emergence of the Newtonian dynamical scheme of inertia, momentum, and energy of a particle of matter, as the approximate translation into the Newtonian frame of a form of Action $-\int mc ds$ in the Minkowskian fourfold which is of a simplicity almost geometric in character. If gravitation should refuse to come in, this striking concatenation of Newtonian dynamics (with modifications for very high velocities) into the simplest possible fourfold quasi-geometrical Action would still persist, in its simpler homogeneous form, in so far as the masses of atoms can be taken to arise from inertia of their local electrodynamic fields. But gravitation would stand outside it as a residual phenomenon, though in essence hardly more unexplained than it is now.

On the other hand, even if there were complete failure of the astronomical tests, all of them very delicate and precarious, as may appear now to be possible, the theory would retain its position as a remarkable provisional consolidation of the field of physical activity, until some more physical explanation including the necessity of gravitation has been formulated, perhaps by its aid.

Summary.—If nothing has been overlooked in this presentation, fundamental consequences seem to be involved. The inclusion of a field of gravitation in the electrodynamic scheme, by making the fourfold extension variable within a principle of dynamical Action, extended throughout it, remains consistent. A stress-tensor, invariant though imperfectly as before, can be duly balanced throughout the field and around the masses; for that result is involved in the Action principle. But the gravitational warping of the fourfold pseudo-space, due to given inertial masses, and all that depends on it, are halved, including the disturbing effects on light. In the Einstein mixed field, electric and gravitating, the balance of the stress-tensor is not disturbed by this halving of the constant of gravitation in it. The orbit of a planet is however no longer a straightest path, determined everywhere locally, in the fourfold extension, as formulated by electrodynamics and its optical rays but modified slightly by gravitation: though it would be so approximately in a different fourfold, but one outside the group for which electrodynamic relativity would subsist. Gravitation therefore cannot be absorbed in the spatial frame of reference. The "principle of equivalence," which in its application has involved only the postulate that light is affected by a field of gravitation in the same manner as by the field of

universal acceleration of matter which it produces, would, along with the implication of a vacuum, not be true. But that postulate seems to have reference to a latent Newtonian frame, for in the fourfold representation the ideas both of gravitation and of acceleration are transcended: having served as a provisional stimulus and a signpost towards a new region to be explored, it might in any case have disappeared from a completed synthesis. However these questions may be settled, the new theories do not (as yet) explain gravitation: the question why it exists at all in the world is as inscrutable still as it was to Newton: but one way has been exhibited along which it can be very slightly and consistently modified so as to bring it into correlation with electrodynamic theory. The same procedure of conscious reversion to practical Newtonian frames of reference is used to explore cognate problems, such as the question of what precisely can be meant by the assertion that the energy of translatory motion of a body whose mass is intrinsic adds to its inertia, and whether such energy gravitates. And other fundamental questions are briefly considered from the same objective point of view.

[Pressure of time in printing prevents more than an abstract of the additional part referred to in footnote, p. 244. The proposition that orbits could still, on Action theory, be determined separately by formulæ of type $-\delta(m_c ds_r) = 0$ in a fourfold extension involving 2γ , while the extension for electrodynamics and optics is a different one involving γ , is general and not confined to the problem of two bodies: but it is otiose, because the object of the theory is to consolidate these two domains. In the electrodynamic fourfold the orbit of a material particle is held to be determined directly by the positions of the other masses in the field, just as the orbit of an ion is already admitted to be determined by the other charged bodies that are present. The approximate expression on p. 252 for the Action, of fourfold type, in the case of two masses can be transformed readily in the known manner to new coordinates, those of their centre of mass and those of their relative position: in the result these sets of variables are found to be separated, and an expression for the Action of the relative orbit thus appears, involving (as Newton proved) a factor $2\gamma(m_1 + m_2)$ instead of $2\gamma m_1$ for the mass m_2 , whereas the fourfold extension that is the basis of the Action theory, in which optics also must be evolved, involves γm_1 for the field of m_1 . The necessity of an underlying uniform Minkowskian fourfold for final reference after the manner of an æther, is discussed.]

Spectra of Alkali Amalgams.

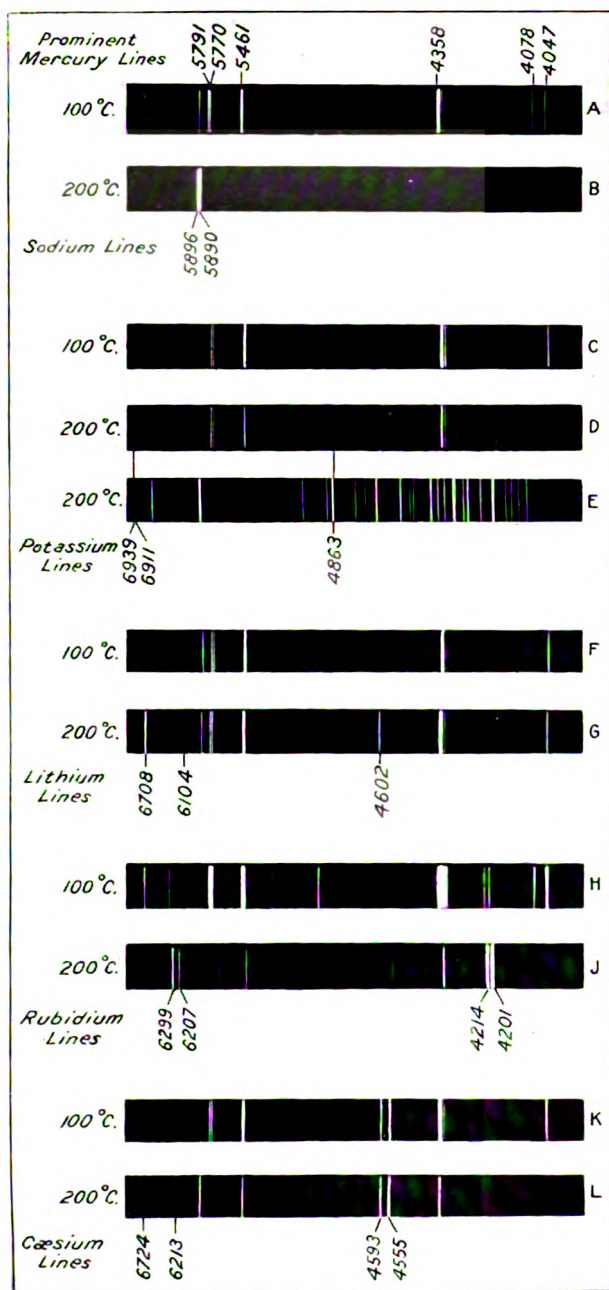


FIG. 1.



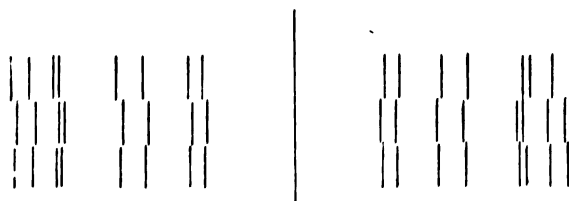
Pd.

FIG. 2.



H₂ absorbed.

FIG. 3.



THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

FEBRUARY 1923.

XXIII. *The Early Stages of a Submarine Explosion.*
By H. LAMB, F.R.S.*

THE theory of the collapse of a spherical bubble in water has been given by Besant† and Rayleigh‡. The cognate problem of the expansion of a spherical cavity owing to the pressure of an included gas is of some interest as the nearest approach we can make at present to the case of a submarine explosion. The representation is defective in various ways, some of them obvious enough, but the study of the problem as thus idealized may still have some value as indicating at all events the order of magnitude of the results to be expected in certain cases. For very intense explosions the results are subject to considerable qualification, as will appear.

Let us imagine that a quantity of gas is liberated instantaneously in a spherical cavity in an unlimited mass of liquid initially at rest. The liquid is assumed for the present to be incompressible, and the density of the gas at each instant to be uniform. Let R_0 be the initial radius of the cavity, R its radius after a time t , p_0 the initial pressure of the gas, ρ the density of the liquid. The velocity potential

* Communicated by the Author.

† Hydromechanics, p. 198 (1867).

‡ Phil. Mag. vol. xxxiv. p. 94 (1917); Scientific Papers, vol. vi. p. 504.

in the liquid at a distance r from the centre of the cavity is accordingly

$$\phi = R^2 \dot{R}/r, \dots \dots \dots (1)$$

since this makes $-\partial\phi/\partial r = \dot{R}$ for $r = R$. The formula for the pressure is therefore

$$\frac{p}{\rho} = \frac{\partial\phi}{\partial t} - \frac{1}{2} \left(\frac{\partial\phi}{\partial r} \right)^2 = \frac{R^2 \ddot{R} + 2R\dot{R}^2}{r} - \frac{R^4 \dot{R}^2}{2r^4}, \dots \dots (2)$$

provided the pressure at infinity is relatively negligible. The initial acceleration of the radius is therefore c_0^2/R_0 , where

$$c_0 = \sqrt{(p_0/\rho)}. \dots \dots \dots (3)$$

This velocity c_0 determines the rapidity with which the subsequent changes take place. If, for example, the initial pressure be 1000 atmospheres, or say $p_0 = 10^9$ C.G.S. we have in the case of water $c_0 = 3 \cdot 16 \times 10^4$. For an initial pressure of 10,000 atmospheres, $c_0 = 10^5$.

If we assume the gas to follow Boyle's law, so that

$$p/p_0 = (R_0/R)^3 \dots \dots \dots (4)$$

for $r = R$, we have, putting $r = R$ in (2),

$$R\ddot{R} + \frac{3}{2}\dot{R}^2 = c_0^2 \left(\frac{R_0}{R} \right)^3, \dots \dots \dots (5)$$

$$\text{or} \quad \frac{d}{dt} (R^3 \dot{R}^2) = 2c_0^2 R_0^3 \frac{\dot{R}}{R}. \dots \dots \dots (6)$$

$$\text{Hence} \quad \frac{\dot{R}^2}{c_0^2} = 2 \left(\frac{R_0}{R} \right)^3 \log \frac{R}{R_0}. \dots \dots \dots (7)$$

This result may also be obtained at once by equating the kinetic energy of the liquid to the work done by the gas in expanding*.

It easily follows from (5) and (7) that $\dot{R}$ is a maximum when $R/R_0 = \sqrt[3]{e} = 1 \cdot 396$, and that this maximum is $\cdot 495c_0$.

The volume of the gas, on the other hand, expands at an ever-increasing rate; we have, in fact, from (6) and (7)

$$4\pi R^2 \dot{R} = 4\pi R_0^2 c_0 \left(\frac{2R}{R_0} \log \frac{R}{R_0} \right)^{\frac{1}{2}}, \dots \dots \dots (8)$$

which increases continually with R .

* Cf. Rayleigh, *loc. cit.*

Substituting in (2) from (5) and (7) we find, for the pressure at any point in the liquid,

$$\frac{p}{p_0} = \frac{R_0^3}{R^3 r} \left\{ 1 + \left(1 - \frac{R^3}{r^3} \right) \log \frac{R}{R_0} \right\}. \quad (9)$$

To complete the solution we write

$$R = R_0 e^{kx^2}, \quad (10)$$

so that (7) becomes

$$e^{5kx^2} \left(\frac{dx}{dt} \right)^2 = \frac{c_0^2}{2kR_0^3}. \quad (11)$$

Hence, putting $k = \frac{2}{5}$, we have

$$\frac{c_0 t}{R_0} = \frac{2}{\sqrt{5}} \int_0^x e^{x^2} dx, \quad (12)$$

where
$$x = \sqrt{\left(\frac{5}{2} \log \frac{R}{R_0} \right)}. \quad (13)$$

This gives the time taken by the radius of the cavity to attain any assigned value R .

The integral in (12) has been tabulated by Dawson* for values of x ranging from 0 to 2 at intervals of .01. For large values of x we might use the asymptotic formula†

$$\int_0^x e^{x^2} dx = e^{x^2} \left(\frac{1}{2x} + \frac{1}{2^2 x^3} + \frac{1 \cdot 3}{2^3 x^5} + \frac{1 \cdot 3 \cdot 5}{2^4 x^7} + \dots \right).$$

The annexed Table I. is based on Dawson's results. The fifth column gives the ratio in which the pressure of the gas is diminished, whilst the last column shows the variation of the pressure in the liquid at a point so distant that the term R^3/r^3 in the inner bracket of (9) may be neglected. In the diagram the values of R/R_0 , $\dot{R}/c_0$, and $pr/p_0 R_0$ are plotted (on different scales) against $c_0 t/R_0$ as abscissa, the ordinates being respectively R/R_0 , $10\dot{R}/c_0$, and $10pr/p_0 R_0$.

If instead of Boyle's law we adopt the adiabatic law of expansion, we have in place of (4)

$$p/p_0 = (R_0/R)^{3\gamma} \quad (14)$$

for $r = R$. Hence (5) is replaced by

$$R\ddot{R} + \frac{3}{2}\dot{R}^2 = c_0^2 \left(\frac{R_0}{R} \right)^{3\gamma}, \quad (15)$$

* Proc. Lond. Math. Soc. (1) vol. xxix. p. 519 (1898).

† Stokes, Camb. Trans. vol. x. p. 181 [Papers, vol. iv. p. 78].

TABLE I.

$x.$	$c_0 t/R_0.$	$R/R_0.$	$\dot{R}/c_0.$	$R_0^3/R^3.$	$pr/p_0 R_0.$
0	0	1.000	0	1.000	1.000
.1	.090	1.004	.089	.988	.996
.2	.181	1.016	.175	.953	.984
.3	.277	1.037	.257	.897	.965
.4	.378	1.066	.325	.826	.936
.5	.488	1.105	.385	.741	.901
.6	.609	1.155	.432	.649	.858
.7	.745	1.217	.466	.555	.807
.8	.903	1.292	.487	.463	.752
.9	1.087	1.383	.495	.378	.692
1.0	1.330	1.492	.491	.301	.629
1.1	1.578	1.623	.476	.234	.563
1.2	1.915	1.779	.452	.178	.498
1.3	2.343	1.966	.422	.132	.433
1.4	2.899	2.190	.386	.095	.372
1.5	3.634	2.460	.348	.067	.314
1.6	4.627	2.784	.304	.046	.261
1.7	5.996	3.177	.269	.031	.214
1.8	7.919	3.655	.230	.020	.172
1.9	10.68	4.238	.195	.013	.124
2.0	14.72	4.953	.162	.008	.106

whence

$$\frac{\dot{R}^2}{c_0^2} = \frac{2}{3(\gamma-1)} \left\{ \left(\frac{R_0}{R} \right)^3 - \left(\frac{R_0}{R} \right)^{3\gamma} \right\} \dots (16)$$

The maximum of $\dot{R}$ now occurs when

$$(R/R_0)^{3\gamma-3} = \gamma, \quad \dots \dots \dots (17)$$

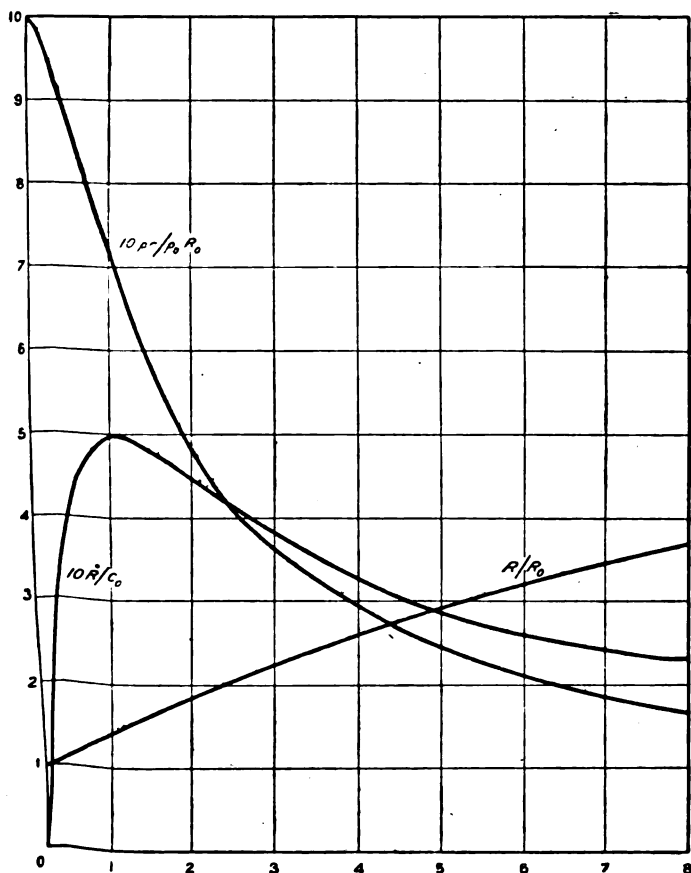
and is given by

$$\frac{\dot{R}^2}{c_0^2} = \frac{2}{3\gamma^{1/(\gamma-1)}} \dots \dots \dots (18)$$

The pressure in the liquid, as found from (2) and (15), is

$$\begin{aligned} \frac{p}{p_0} = \frac{1}{3(\gamma-1)} \frac{R}{r} \left\{ (3\gamma-4) \left(\frac{R_0}{R} \right)^{3\gamma} + \left(\frac{R_0}{R} \right)^3 \right\} \\ - \frac{1}{3(\gamma-1)} \frac{RR_0^3}{r^4} \left\{ 1 - \left(\frac{R_0}{R} \right)^{3\gamma-3} \right\}, \quad \dots (19) \end{aligned}$$

the second line being relatively unimportant at a distance from the centre.



The integration of (16) cannot as a rule be effected analytically. An exception worth notice occurs, however, in the case of $\gamma = \frac{4}{3}$. Writing

$$R/R_0 = 1 + z, \quad \dots \quad (20)$$

we have then

$$(1+z)^3 \frac{dz}{dt} = \frac{c_0}{R_0} \sqrt{2z}, \quad \dots \quad (21)$$

whence

$$\frac{c_0 t}{R_0} = \sqrt{2z} \left(1 + \frac{2}{3}z + \frac{1}{5}z^2 \right). \quad \dots \quad (22)$$

It may be remarked that this same formula would be obtained on the isothermal hypothesis if we were to neglect the term depending on the square of the velocity in the general expression (2) for the fluid pressure. The correct isothermal hypothesis gives for *small* values of z

$$\frac{c_0 t}{R_0} = \sqrt{(2z)(1 + \frac{1}{2}z + \dots)}. \quad (23)$$

The maximum of $\dot{R}$, when $\gamma = \frac{4}{3}$, corresponds to $R/R_0 = \frac{4}{3}$, and is $\cdot 459c_0$. The pressure at a distance is given by

$$\frac{p}{p_0} = \frac{R_0}{r} \left(\frac{R_0}{R} \right)^2, \quad \dots \quad (24)$$

approximately.

The following Table II. is derived from (22) and (24). It is unnecessary to plot the results, since the curves will have the same *general* form as on the former hypothesis.

TABLE II.

R/R_0	$c_0 t/R_0$	$\dot{R}/c_0$	$(R_0/R)^2$	$pr/p_0 r_0$
1.0	0	0	1.000	1.000
1.1	.478	.369	.751	.826
1.2	.722	.439	.579	.676
1.3	.943	.458	.455	.592
1.4	1.162	.456	.364	.510
1.5	1.383	.445	.296	.444
1.6	1.612	.428	.244	.391
1.7	1.850	.409	.204	.346
1.8	2.101	.391	.171	.309
1.9	2.364	.372	.146	.277
2.0	2.640	.354	.125	.250
2.1	2.930	.336	.108	.227
2.2	3.235	.320	.094	.207
2.3	3.555	.305	.082	.189
2.4	3.891	.291	.072	.174
2.5	4.244	.277	.064	.160
2.6	4.613	.265	.057	.148
2.7	4.999	.253	.051	.137
2.8	5.404	.242	.046	.128
2.9	5.827	.232	.041	.119
3.0	6.266	.222	.037	.111
4.0	11.76	.153	.016	.063
5.0	19.42	.113	.008	.040

Since cooling of the gas by expansion and consequent diminution of pressure are now taken into account, the

changes take place more slowly than in the previous case.

As a concrete illustration, let us suppose the initial diameter of the cavity to be 1 metre, and the initial pressure p_0 to be 1000 atmospheres. Putting $\rho=1$, $c_0=3.16 \times 10^4$, we find from Table II. that the radius is doubled in $\frac{1}{2.50}$ of a second, and multiplied five-fold in about $\frac{1}{3.0}$ sec. The initial acceleration of the radius is 2.00×10^7 cm./sec.², showing that the neglect of gravity in the early stages of the motion is amply justified. The maximum of $\dot{R}$ occurs when $R=\frac{4}{3}R_0$, $t=.0016$ sec., and is about 145 metres per second, or about one-tenth the velocity of sound in water.

If the initial pressure p_0 had been 10,000 atmospheres, the radius of the cavity would be doubled in about $\frac{1}{7.50}$ sec., and multiplied five-fold in $\frac{1}{10.0}$ sec. The maximum of $\dot{R}$ would now be 460 metres per sec.

A more difficult question remains as to how far the results are modified by the compressibility of the water. It would appear that so long as the velocity which we have denoted by c_0 is small compared with the velocity (c) of sound-waves in the water the effect would not be very great, although the time-scale would be somewhat extended. But with initial pressures of the order of 10,000 atmospheres in our previous example the effect would become appreciable. In the case of a submarine mine the initial pressures may greatly transcend this amount, with the result that the velocities communicated to the adjacent water may exceed the ordinary velocity of sound, even when allowance is made for the diminution of compressibility with increase of pressure. Our theory then ceases to have any very close relation to the facts.

The accurate equations of motion of spherical waves in a compressible medium are easily formulated, although a solution seems at present hopeless. Assuming that p is a definite function of ρ we write

$$\omega = \int_{\rho_1}^{\rho} \frac{dp}{\rho} = \int_{\rho_1}^{\rho} c^2 \frac{d\rho}{\rho}, \quad \dots \quad (25)$$

where ρ_1 is the undisturbed density, and

$$c^2 = dp/d\rho. \quad \dots \quad (26)$$

We have then the dynamical equation

$$\omega = \frac{\partial \phi}{\partial t} - \frac{1}{2} \dot{\eta}^2, \quad \dots \quad (27)$$

where q is the velocity, and the kinematical relation

$$\frac{1}{\rho} \frac{D\rho}{Dt} = \nabla^2 \phi. \quad (28)$$

Hence

$$\frac{D\varpi}{Dt} = \frac{c^2}{\rho} \frac{D\rho}{Dt} = c^2 \nabla^2 \phi. \quad (29)$$

We may eliminate ϖ , so far as it appears explicitly, between (27) and (29). The result is rather long, but in the case of spherical waves it reduces to

$$\frac{\partial^2 \phi}{\partial r^2} + \frac{2}{r} \frac{\partial \phi}{\partial r} = \frac{1}{c^2} \left\{ \frac{\partial^2 \phi}{\partial t^2} - 2 \frac{\partial \phi}{\partial r} \frac{\partial^2 \phi}{\partial r \partial t} + \left(\frac{\partial \phi}{\partial r} \right)^2 \frac{\partial^2 \phi}{\partial r^2} \right\}, \quad (30)$$

as is easily verified. Since c is in general a function of ρ , this equation has to be combined with (28).

Some estimate of the importance of the expression on the right-hand is obtained if we substitute the values of ϕ which were found on the hypothesis of incompressibility, just as if we were attempting a second approximation. Taking, for instance, the formulæ (1) and (16) with $\gamma = \frac{4}{3}$, we get

$$- \frac{2c_0^2}{c^2} \frac{\dot{R}}{r} \left\{ \frac{R_0^3}{R^3} + \frac{R_0^3}{r^3} - 2 \frac{R^6}{r^6} \left(\frac{R_0^3}{R^3} - \frac{R_0^4}{R^4} \right) \right\},$$

Since the same hypothesis makes the terms $\partial^2 \phi / \partial r^2$ and $2\partial \phi / r \partial r$ equal to $\pm 2R^2 \dot{R} / r^3$, it would appear that, provided the ratio c_0^2 / c^2 is small, the second member of (30) is negligible in the neighbourhood of the boundary ($r=R$). The argument is of course far from rigorous, but it is of a kind to which we are often constrained to have recourse in mathematical physics.

At a sufficient distance from the origin the ordinary theory of sound-waves, in which terms of the second order are neglected, becomes applicable. We have then as usual

$$\phi = \frac{1}{r} f\left(t - \frac{r}{c}\right), \quad (31)$$

$$\frac{p - p_1}{\rho} = \frac{\partial \phi}{\partial t} = \frac{1}{r} f'\left(t - \frac{r}{c}\right), \quad (32)$$

$$q = - \frac{\partial \phi}{\partial r} = \frac{1}{r^2} f\left(t - \frac{r}{c}\right) + \frac{1}{cr} f'\left(t - \frac{r}{c}\right), \quad (33)$$

where c is now regarded as constant. As regards the pressure, the only deviation from the case of incompressibility is that changes are propagated, not instantaneously, but with the finite velocity c , with of course the usual attenuation due to increase of distance from the source. The law of transmission of velocity is, however, modified. Except for the "retardation" r/c the first term in the value of q is the same as if the fluid were incompressible, whilst the additional term is equal to $(p-p_1)/\rho c$. The relative importance of the two terms depends on the ratio

$$\tau = f\left(t - \frac{r}{c}\right) \bigg| f'\left(t - \frac{r}{c}\right), \quad . \quad . \quad . \quad (34)$$

which is of the nature of a time. This (variable) time measures the degree of slowness with which the strength of the virtual source $f(t)$ was changing at the instant when it started the waves which in time t have travelled the distance r . Writing (33) in the form

$$q = \frac{p-p_1}{\rho c} \left(\frac{c\tau}{r} + 1 \right), \quad . \quad : \quad . \quad . \quad . \quad (35)$$

it is seen that the first term preponderates when $c\tau$ is large compared with r , and is relatively insignificant in the opposite extreme. These relations are familiar in the case of a periodic source of sound, where τ may be identified with the period. Sufficiently near the source the motion is practically the same as if the fluid were incompressible. And the range of r to which this statement applies is greater, the lower the frequency.

In the present problem the value of τ is infinitesimal at the front of the advancing wave, where there is an abrupt change of conditions. We have there

$$q = (p-p_1)/\rho c, \quad . \quad . \quad . \quad . \quad . \quad (36)$$

simply, as is otherwise evident from consideration of the transfer of momentum.

XXIV. *Physical Constants and Ultimate Rational Units.* By
GILBERT N. LEWIS, *Professor of Chemistry, The University
of California* *.

A NEW empirical law usually involves one or more constants, and if the law appears to be general and fundamental these constants are called constants of nature. The discovery of every such constant is indeed a milestone in the progress of science. Nevertheless, to call these quantities natural constants is a characteristically human attempt to shift responsibility. Adopting an old-fashioned phraseology, there is nothing nature abhors more than an arbitrary number which possesses no intrinsic meaning. Perhaps, therefore, it would be better to call them unnatural constants, and reserve the term natural constants for simple numbers like 2 or π .

If we accept the view that is set forth in this paper, and consider that every physical constant indicates some flaw in our scientific system, it becomes as useful a scientific service to eliminate these constants as to discover them. Such an elimination has often been secured by a mere change in the units of measurement; and thus by the two-fold process of discovering new constants and then of reducing these constants to unity or simple numbers, by a change in the system of units, we are progressing toward a more natural or "rational" set of physical units.

The Metric or C.G.S. System.

The units of the metric system are completely arbitrary. Certainly there is nothing fundamental to physics in the period of rotation of the earth, or the dimensions of the earth, or the density of an arbitrarily chosen substance at an arbitrarily chosen temperature and pressure. On the other hand, the introduction of the c.g.s. system represented in two respects a great advance toward the adoption of natural units.

Whether or not it is the best system of counting, the civilized world has definitely adopted decimal numbers; and it was therefore very desirable to replace those systems of weights and measures, inherited from prehistoric civilizations which used other (and possibly better) number systems, by a set of units which stand in simple decimal ratio to one another.

From the standpoint of physics, a far greater advance was

* Communicated by the Author.

secured by the c.g.s. system in fixing the secondary units, such as those of momentum and energy. While the centimetre, gram and second are entirely arbitrary, the ratios between them and the secondary or derived units are made natural ratios and not arbitrary ones which involve a series of meaningless constants. By this one step modern physical equations have been vastly simplified.

The Mechanical Equivalent of Heat.

When it was discovered that a certain amount of work lost in friction always produced the same quantity of heat, a natural constant was thereby discovered, and the custom has not entirely disappeared of putting this number, the so-called mechanical equivalent of heat, into every equation involving mechanical and thermal quantities. But it is one of the signal accomplishments of the theory of energy that heat and work are now regarded as different manifestations of the same fundamental entity, and are therefore expressed in terms of the same unit. Accordingly it is now the custom to write rational thermodynamic equations without this awkward constant.

However, we must not confuse two distinct mental operations which are involved in such a case. The mere fact that two entities are expressed in the same unit does not force us to regard them as identical. Angular velocity has the dimensions of frequency, and indeed, in the case of uniform rotation, a given angular velocity implies a definite frequency of rotation. But the two ideas are distinct, notwithstanding the fact that the two quantities may be expressed in the same units. So a person might dispute the theory of energy, that work and heat are the same entity, but no one could fail to recognize the convenience of expressing work and heat in the same units.

The Constant of Dulong and Petit, and the Gas Constant.

An important physical constant was the one discovered by Dulong and Petit—namely, the heat capacity per gram atom of a solid element. One of Boltzmann's valuable services to science consisted in showing that the constant of Dulong and Petit is merely the gas constant multiplied by 3.

We now see, moreover, that the existence of the gas constant itself is due to the use of units which are not rationally derived from the c.g.s. system. Thus the constant R is defined as the pressure exerted by 32 grams of oxygen when multiplied by the volume and divided by the absolute temperature. We

now know that 32 grams of oxygen contains $N (=6.06 \times 10^{23})$ molecules, and it is evidently less arbitrary to write

$$PV = n \frac{R}{N} T = nkT,$$

where n represents the number of molecules, and k is called the molecular gas constant.

When PV is expressed in ergs and T is expressed in terms of the Celsius degree, $k = 1.372 \times 10^{-16}$. Now the value of the degree was decided upon without reference to the c.g.s. system, and might as well have been taken of such magnitude as to make the molecular gas constant unity. Complete justification for such a choice is seen in the fact that in the radiation equations of Rayleigh and Planck, which have no direct relation to the properties of gases or of molecules, T is accompanied by the same constant k . A degree which is $1/1.372 \times 10^{-16}$ times as great as the Celsius degree we may therefore call the c.g.s. unit of temperature.

A further consequence of this step deserves comment. The whole theory of the dimensionality of physical quantities has been obscured by the existence of physical constants, to which dimensions are often assigned. Now while it might seem reasonable to assign dimensions to R or k , it would be highly inconvenient to give dimensions to a pure number and especially to unity, which does not even appear in the physical equations. We are thus forced to give c.g.s. temperature the dimensions of energy, and express it in ergs.

Electric and Magnetic Units.

In the development of electromagnetic theory numerous constants might have entered if, for example, the earth had been taken as a unit magnet, or if the unit of charge had been defined as the amount to which some condenser is charged by a Grove cell. On the contrary, every effort was made to choose units which would be rational in the c.g.s. system. Nevertheless, there arose two systems of measurement, the electrostatic and the electromagnetic, and the ratio of the two became a new constant of nature. Later, one of the prodigious successes of Maxwell's theory consisted in the recognition of the identity between this constant and another important constant— c , the velocity of light.

Throughout electromagnetic theory we find numerous equations in which the constant c appears, and always with the time t and to the same power as t . It is evident that the

appearance of this constant is not due to any faulty application of the c.g.s. method, but rather to the arbitrary choice of the primary c.g.s. units themselves.

The Rational Unit of Time.

Especially through the development of the new kinematics of Einstein we are forced to the inevitable conclusion that the most rational choice of temporal and spatial units would be one whereby the velocity of light would be made equal to unity. If provisionally we retain the centimetre as the unit of length, the unit of time must be made 2.999×10^{10} times as small as the second.

Here, again, making the constant unity requires us for convenience to make it dimensionless, and we therefore call the new unit of time the centimetre, and we write 1 sec. $= 2.999 \times 10^{10}$ cm.

Once more it is to be pointed out that the use of the same unit for time and for length does not mean that we need regard time and space as completely indistinguishable. Indeed, any one conversant with the 4-dimensional geometry of relativity, while recognizing the great convenience of a common unit, must also recognize that between the concepts of time and space there is a fundamental distinction which relativity does not remove.

Units of Mass, Momentum, and Energy.

A further consequence of relativity is that the energy and the mass of a body vary proportionally to one another, and that the factor of proportionality is the square of the velocity of light. Moreover, if we take velocity as dimensionless, mass and energy have the same dimensions, and therefore we may say that 1 gm. $= c^2$ ergs. With the new unit of time the rational unit of both energy and momentum is the gram.

The Theory of Ultimate Rational Units.

Starting with the four units of length, time, mass, and temperature, we have seen that by making the molecular gas constant and the velocity of light equal to unity, the number of units may be reduced to two—namely, the centimetre and the gram. It is evident that by using in the same way two other fundamental constants, these two arbitrary units might also be replaced by less arbitrary ones.

Such a system of units was indeed suggested by Planck *, who proposed to make equal to unity, not only k and c , but

* Planck, *Vorlesungen über die Theorie der Wärmestrahlung*.

also h , the constant of the Planck radiation formula, and f , the constant of gravitation. This would give new units for length, time, mass, and temperature "which independently of special bodies or substances would retain their significance for all times and for all civilizations, even those beyond the terrestrial and the human."

While granting the presumptive truth of this statement, the question still remains as to whether the constants chosen in this refixing of the four units are the best ones, and used in the best way. Such a choice would, as far as was apparent, eliminate only four of our physical constants, leaving numerous others which might perhaps equally well have been chosen for the determination of the primary units.

It was at this point that Dr. E. Q. Adams and I advanced our theory of ultimate rational units*. According to this theory there is possible a set of units in terms of which all universal constants (and not merely those which are employed in defining the units) will be reduced to simple numbers. The system of ultimate rational units will be the one in which these numbers are in general the simplest.

In attempting, therefore, to determine the new units of length and mass, we must look for two relations which are as simple and as inevitable as those which we have used to eliminate the arbitrary units of temperature and of time. These two relations will then enable us to replace the gram and the centimetre as well as the units of time and temperature by ultimate rational units.

Hitherto we have been able to decide only upon one such relation, which therefore merely permits us to express all other units in terms of a single one. For this one we shall provisionally retain the centimetre.

The New Unit of Mass or Energy.

It seemed to us that the most fundamental of the outstanding constants was the elementary charge—that is, the charge possessed by an electron or by a univalent positive ion, and we chose the fundamental constant $(4\pi e)^2$, where e is the electron charge in ordinary electrostatic units, namely 4.774×10^{-10} . Now, in ordinary units the square of a charge has the dimensions of energy times length; and if we take new units of mass and energy such that $(4\pi e)^2$ is unity and dimensionless, then the new unit of energy or mass becomes the reciprocal centimetre, and we may write

$$1 \text{ erg} = 2.779 \times 10^{16} \text{ reciprocal centimetres;}$$

$$1 \text{ gram} = 2.499 \times 10^{37} \text{ reciprocal centimetres.}$$

* Lewis and Adams, Phys. Rev. iii. p. 92 (1914).

Thus energy and mass acquire the dimensions of curvature, or frequency, or acceleration. Indeed, it will be noted that we have now reduced all physical quantities to the dimensions of a power of length. Although this change seems radical, I claim emphatically that we are introducing no new element into the theory of physical dimensions; what we do is no more than has been repeatedly done before in other cases, ever since the introduction of the c.g.s. system.

The Constant of Stefan's Law.

The first success of the theory of ultimate rational units came in the calculation of the constant of Stefan's law. According to this law, if E/V is the energy-density of a hohlraum, $E/V = aT^4$. We concluded that when these quantities were all expressed in terms of ultimate rational units, the constant a would become unity. We were thus able to calculate a value of Stefan's constant, claiming a much higher accuracy than the values which had then been obtained by experiment.

In the two years preceding the publication of our paper, seven determinations of this quantity had been made, as shown in Table I. The results were by no means concordant, the average deviation from the mean being 3·8 per cent. As against the average of 5·81 (for $ac/4$), our calculated value was 5·70, and we predicted that more careful determinations would yield this value. Recently, after a thorough reinvestigation of the subject, Coblenz has obtained the value $5·72 \pm 0·012$, in almost perfect accord with the value which we calculated.

TABLE I.

Stefan's Constant (1912-1913).

Author.	$(ac/4) \times 10^5$.
Shakespear	5·67
Gerlach	5·80
Kurlbaum	5·45
Puccianti ...	5·96
Westphal	5·54
Keene.....	5·89
Fery and Drecq	6·33
Average	5·81
Average deviation 3·8 per cent.	
Calculated (U.R.U.).....	5·70
Coblenz * (1917)	$5·72 \pm 0·012$

* Coblenz, Proc. Nat. Acad. Sci. iii. p. 504 (1917)

Planck's Constant.

With an accurate value of Stefan's constant, it was possible to obtain therefrom the constant of Planck, assuming the correctness of his radiation formula. In ordinary units the value so calculated was 6.560×10^{-27} . At that time the value obtained in the Bureau of Standards by Coblentz was 6.615, differing from our calculated value by 0.055. Recent determinations, however, have almost completely verified the one which we calculated. Later work by Coblentz* led to the value 6.557, and the mean* of many recent determinations of this quantity is 6.554, differing by only 0.003 and 0.006 from the value we predicted.

Unless, therefore, we are to assume a bizarre coincidence, the recent determinations of the constants of Stefan and Planck furnish a striking justification of the ideas which Dr. Adams and I advanced.

The Entropy of a Monatomic Gas.

In classical thermodynamics the theory of an ideal monatomic gas was given by the expression

$$S = \frac{3}{2}R \ln T + R \ln V + \text{const.},$$

and the constant was regarded as undetermined and undeterminable. With the advent of the third law of thermodynamics, and especially in consequence of the work of Planck, we are now able to assign a definite finite entropy to every substance, and to calculate these entropies from simple measurements.

When this was done it was observed by Sackur† that the numerical values obtained for the entropy of monatomic gases permitted the constant in the above equation to be broken up into two terms, one of which depends only upon the atomic weight, and the other of which is a universal constant which is independent of the nature of the gas. Thus, if W is the atomic weight,

$$S = R \ln (T^{3/2} W^{3/2} V) + C,$$

$$S = R \ln (C' T^{3/2} W^{3/2} V),$$

where $R \ln C' = C$.

Now, if we replace W and V by the mass of one molecule and the volume occupied per molecule, then convert T into c.g.s. units of temperature, and finally reduce everything to

* See Birge, *Phys. Rev.* xiv. p. 361 (1919).

† Sackur, *Ann. Phys.* xxxvi. p. 598 (1911); xl. p. 67 (1913).

our new units, it is a consequence of the theory of ultimate rational units that C and C' must be pure numbers, and probably simple numbers. The only way in which they can both be made simple numbers is to assume that in the new units $C'=1$ and $C=0$. Accepting these values and converting back to ordinary units, we find

$$C' = \frac{k^{3/2} r^3}{N^{5/2} (4\pi e)^6} = 3.252 \times 10^{-3}.$$

Thus with the aid of a simple deduction from the theory of ultimate rational units, and with no other information whatsoever, we may calculate the entropy of any monatomic gas. Of the several monatomic gases whose entropies have been experimentally determined, there are only four for which the data are at all accurate. The experimental values for these four gases (expressed in calories per degree), together with those calculated from the equation which I have just given, are shown in Table II. The agreement is remarkable, being in every case within the limits of possible experimental error. As in the previous calculation of the constant of Stefan's law, the constants employed in the present calculation are sufficiently well known to give the calculated values an accuracy at least ten times that of any present measured value. Here, again, I venture to predict that new experimental determinations will bring the entropies constantly nearer to those calculated from the equation here given.

TABLE II.

Entropy* of Four Monatomic Gases at 25° C. and 1 atmos.

	Exp.	Calc.
He	29.2	29.8
A	36.4	36.7
Cd	40.0	39.8
Hg	41.3	41.5

The atomic weights of these four gases range from 4 to 200. Moreover, there is evidence† that within the rather wide limits of experimental error the same equation is applicable to the electron with its very much smaller mass. This conclusion has permitted an interesting investigation of stellar spectra in the hands of Saha‡.

* These values are taken from a paper by Lewis, Gibson, and Latimer, *J. Am. Chem. Soc.* xlv. p. 1008 (1922).

† See Laue, *Jahrb. Radioakt. Elektronik.* xv. p. 257 (1918). Tolman, *J. Am. Chem. Soc.* xliii. p. 1592 (1921).

‡ Saha, *Phil. Mag.* xl. p. 72 (1920).

Phil. Mag. S. 6. Vol. 45. No. 266. Feb. 1923.

T

On account of the unfamiliarity of the ideas which we are dealing with, and lest anyone believe that we are here confronted by a mere numerical coincidence such as occasionally appears in scientific calculations, it may be of interest to describe very briefly the manner in which the value of the constant was first obtained. When I became convinced through a paper by Tolman* that Sackur's equation expressed an exact law of nature (except for the values which he, and later Tetrode†, assigned to the constant), I predicted that this constant (C) would be equal to zero in ultimate rational units. At that time I had no idea, except one based on the theory of ultimate rational units, that this prediction would be correct even in order of magnitude. Indeed, when at the first opportunity I carried out the calculation, I found a discrepancy between theory and experiment involving a factor of 10^{20} . At this point some of my colleagues were inclined to doubt the validity of the theory, but feeling confident that some material error must have entered I repeated the calculation, discovered this to be the case, and obtained the very satisfactory agreement with experiment shown in Table II.

Ultimate Rational Units and the Principle of Similitude.

Dr. Adams and I were struck by the fact that not all, but all of the more universal, physical constants with which we had to deal (except the constant of gravitation) had the dimensions of some power of energy times length (or time) in the c.g.s. units, and were therefore dimensionless in ultimate rational units. This is true of the elementary charge, of Stefan's constant, and of the Planck constant, to which we may now add the constant C of the entropy equation. The idea that this might be a general law has been embodied by Tolman, together with the ordinary theory of dimensionality, in the very interesting theorem which he calls the principle of similitude. This principle is equivalent to a statement that every new fundamental constant will be found to be dimensionless in ultimate rational units.

While we may doubt the complete generality of this principle, it is sure to prove a useful guide to new physical laws.

The Elimination of the Centimetre.

One fundamental constant which is not dimensionless in ultimate rational units is the one discovered by Rydberg. By employing such a constant it is possible to remove the last element of arbitrariness from our system of units. At once

* Tolman, J. Am. Chem. Soc. xlii, p. 1185 (1920).

† Tetrode, *Ann. Phys.* xxxviii, p. 434 (1912).

we might do away with the centimetre, and obtain simplification in our equations, by choosing the mass of the electron as the unit of mass, or h times ν_0 (Rydberg's constant) as the unit of energy. But we shall do well to wait until we can make sure in this step also that the more rational units that we choose are the ones that are likely to prove the best permanently, and may therefore deserve the name of ultimate rational units.

Berkeley, California.

NOTE BY O. J. L.

The publication of a paper does not mean agreement with its contention. I for one hold that an attempt to unify essentially different physical quantities, and obliterate the ratios or constants connecting them, can only result in confusion. *A unit is not unity.* Length and Mass and Time and Energy and Momentum are not the same. Nor is Temperature identical with Energy. Different things sometimes appear to be of the same dimensions, like Work and Moment of force; but there is an element of direction involved even there, and a scalar product differs from a vector product. On the other hand a frequency may rightly be identified with a phase-angle divided by time, which is essentially an angular velocity. So also the identification of Heat and Energy was serviceable, indeed momentous. Any real relation between constants, like $\mu Kc^2=1$ or the expressions of Rydberg and of Planck, is of high value; but the arbitrary elimination of constants, or the attempt to mask them and replace them prematurely by pure numbers, is retrograde.

As to choice of units, that is merely a matter of convenience, not of principle; and a unit of temperature $10^{-16}/1.372$ of a centigrade degree would assuredly not be convenient.

XXV. *The Field of an Electron on Einstein's Theory.*
By S. J. GUNNINGHAM, B.Sc., F.I.A.*

§ 1. *Solution of the Field Equations.*

THE solution of the field equations where the line element is of the form

$$ds^2 = -e^\lambda dr^2 - e^\mu (r^2 d\theta^2 + r^2 \sin^2 \theta d\phi^2) + e^\nu d\tau^2$$

has been given by Nordström † and by Jeffery ‡ for the case $\mu=0$; the field is assumed to be symmetrical in space and static in time.

The solution for the gravitational field of a mass-particle, when $\lambda=\mu$, has been given by Hill and Jeffery §; in this paper it is proposed to give the solution for the field of an electron on this assumption.

The equations of the field, if we suppose matter, apart from the point-mass at the origin, to be absent, are, in the usual notation

$$G_{\mu\nu} = -\frac{8\pi k}{c^4} (E_{\mu\nu} - \frac{1}{2} g_{\mu\nu} E), \quad . \quad . \quad . \quad (1)$$

where k is the constant of gravitation and c the velocity of light.

The values of $G_{\mu\nu}$ that do not vanish are

$$G_{11} = \mu'' + \frac{1}{2}\nu'' + \mu'/r - \frac{1}{4}\mu'\nu' + \frac{1}{4}\nu'^2, \quad . \quad . \quad . \quad (2)$$

$$G_{22} = r\{\frac{1}{2}r\mu'' + \frac{3}{2}\mu' + \frac{1}{2}\nu' + \frac{1}{4}r\mu'^2 + \frac{1}{4}r\mu'\nu'\}, \quad . \quad . \quad (3)$$

$$G_{33} = \sin^2 \theta \cdot G_{22},$$

$$G_{44} = -e^{\nu-\mu} \{\frac{1}{2}\nu'' + \nu'/r + \frac{1}{4}\mu'\nu' + \frac{1}{4}\nu'^2\}. \quad . \quad . \quad (4)$$

Writing the potential vector of the electromagnetic field as

$$\kappa_\mu \equiv (-F, -G, -H, \phi),$$

we have as the only surviving components of the electromagnetic co-variant tensor $F_{\mu\nu}$, the values

$$F_{14} = -F_{41} = -\kappa_4'.$$

For the corresponding contra-variant tensor, we shall have

$$F^{14} = -F^{41} = g^{11}g^{44}F_{14} = e^{-(\mu+\nu)}\kappa_4'.$$

* Communicated by Prof. G. B. Jeffery, M.A., D.Sc.

† Proc. Ac. Amsterdam, vol. xx, p. 1236 (1918).

‡ Proc. Roy. Soc. A, vol. xcix, (1921).

§ Phil. Mag. vol. xli, p. 823 (May 1921).

The mixed electromagnetic energy tensor defined by

$$E_{\nu}^{\mu} = F_{\nu\alpha} F^{\alpha\mu} + \frac{1}{4} g_{\nu}^{\mu} F^{\sigma\tau} F_{\sigma\tau}$$

will then only survive for the values $\mu = \nu = 1$ or 4 , and will be given by

$$E_1^1 = -E_2^2 = -E_3^3 = E_4^4 = \frac{1}{2} e^{-(\mu+\nu)} \kappa_4'^2.$$

The scalar E becomes

$$E = g_{\beta}^{\nu} E_{\nu}^{\beta} = 0, \text{ on summation,}$$

while the co-variant tensor $E_{\mu\nu}$ vanishes except for the values $\mu = \nu$, which are

$$\left. \begin{aligned} E_{11} &= g_{11} E_1^1 = -\frac{1}{2} e^{-\nu} \kappa_4'^2, \\ E_{22} &= g_{22} E_2^2 = \frac{1}{2} r^2 e^{-\nu} \kappa_4'^2, \\ E_{33} &= g_{33} E_3^3 = \frac{1}{2} r^2 \sin^2 \theta e^{-\nu} \kappa_4'^2, \\ E_{44} &= g_{44} E_4^4 = \frac{1}{2} e^{-\mu} \kappa_4'^2. \end{aligned} \right\} \dots (5)$$

From (2), (3), (4), and (5) we have the three equations

$$\mu' + \frac{1}{2} \nu' + \mu' / r - \frac{1}{4} \mu' \nu' + \frac{1}{4} \nu'^2 = \frac{4\pi k}{c^4} \kappa_4'^2 e^{-\nu}, \quad (6a)$$

$$\frac{1}{2} \mu'' + \frac{3}{2} \mu' / r + \frac{1}{2} \nu' / r + \frac{1}{4} \mu'^2 + \frac{1}{4} \mu' \nu' = -\frac{4\pi k}{c^4} \kappa_4'^2 e^{-\nu}, \quad (6b)$$

$$\frac{1}{2} \nu'' + \nu' / r + \frac{1}{4} \mu' \nu' + \frac{1}{4} \nu'^2 = \frac{4\pi k}{c^4} \kappa_4'^2 e^{-\nu}, \quad (6c)$$

together with a fourth equation derived from the equations of the electromagnetic field :

$$\frac{\partial}{\partial x_{\alpha}} (\sqrt{-g} F^{\beta\alpha}) = 0$$

or

$$\frac{\partial}{\partial r} (e^{\frac{1}{2}(\mu-\nu)} r^2 \kappa_4') = 0 \quad \dots (6d)$$

for the determination of μ and ν .

Equation (6d) gives

$$\kappa_4' = \frac{\epsilon}{4\pi} \cdot \frac{1}{r^2} e^{\frac{1}{2}(\nu-\mu)},$$

where $\frac{\epsilon}{4\pi}$ is a constant of integration.

From (6 a) and (6 c) we have

$$\mu'' + \mu'/r - \frac{1}{2}\mu'\nu' - \nu'/r = 0. \quad \dots \quad (7)$$

Adding to (6 b) and substituting for κ_4' from above, we have

$$\mu'' + 2\mu'/r + \frac{1}{4}\mu'^2 = -\frac{\epsilon^2}{4\pi} \frac{k}{c^4 r^4} e^{-\mu},$$

or writing $\rho = \frac{1}{r}$,

$$\frac{d^2\mu}{d\rho^2} + \frac{1}{4}\left(\frac{d\mu}{d\rho}\right)^2 = -\frac{\epsilon^2}{4\pi} \frac{k}{c^4} e^{-\mu}, \quad \dots \quad (8)$$

The solution of this equation is

$$\left(Ae^{4\mu} + \frac{e^2 k}{\pi c^4}\right)^{\frac{1}{2}} = \frac{A}{4}\rho + B,$$

where A and B are the constants of integration.

From considerations at infinity,

$$B = \left(A + \frac{e^2 k}{\pi c^4}\right)^{\frac{1}{2}}.$$

Hence

$$e^{\frac{1}{2}\mu} = 1 + \frac{B}{2r} + \frac{A}{16r^2}$$

or

$$e^{\mu} = (1 + p/r + q/r^2)^2, \quad \dots \quad (9)$$

where

$$p^2 - 4q = \frac{\epsilon^2}{4\pi} \cdot \frac{k}{c^4}.$$

From equations (7) and (6 b), substituting the values obtained for e^{μ} and κ_4' , we have after some reduction

$$\nu' = \frac{2pr^2 + 8qr + 2pq}{(r^2 + pr + q)(r^2 - q)},$$

giving, after integration (the constant of integration being zero),

$$e^{\nu} = \frac{(1 - q/r^2)^2}{(1 + p/r + q/r^2)^3}.$$

It is easily shown that these values for e^{μ} and e^{ν} satisfy equations (6 a), (6 b), and (6 c) identically. Hence the

expression for the line element in this case is

$$ds^2 = -(1 + p/r + q/r^2)^2 (dr^2 + r^2 d\theta^2 + r^2 \sin^2 \theta \cdot d\phi^2) + \left(\frac{1 - q/r^2}{1 + p/r + q/r^2} \right)^2 d\tau^2, \quad (10)$$

where

$$p^2 - 4q = \frac{\epsilon^2}{4\pi} \cdot \frac{k}{c^4}.$$

§ 2. Identification of the Constants.

In order to identify the constants ϵ , p , and q , the equations of motion of a charged particle in the field of the electron will be investigated.

The equations of motion are

$$m' A^\sigma = -\frac{1}{c^2} J^\mu F_{\mu}^\sigma,$$

where J^μ is the current vector

$$\epsilon' \left(\frac{dx_1}{ds}, \frac{dx_2}{ds}, \frac{dx_3}{ds}, \frac{dx_4}{ds} \right),$$

and the acceleration vector

$$A^\sigma = \frac{d^2 x_\sigma}{ds^2} + \{\alpha\beta, \sigma\} \frac{dx_\alpha}{ds} \cdot \frac{dx_\beta}{ds}.$$

On substitution of the values of the surviving Christoffel symbols, we obtain for the equations of motion

$$\begin{aligned} \frac{d^2 r}{ds^2} + \frac{1}{2} \mu' \left(\frac{dr}{ds} \right)^2 - (r + \frac{1}{2} r^2 \mu') \left(\frac{d\theta}{ds} \right)^2 - (r + \frac{1}{2} r^2 \mu') \sin^2 \theta \left(\frac{d\phi}{ds} \right)^2 \\ + \frac{1}{2} c^2 \nu' e^{\nu-\mu} \left(\frac{dt}{ds} \right)^2 = \frac{\epsilon \epsilon'}{4\pi} \cdot \frac{1}{m' c^3 r^2} e^{\frac{1}{2}(\nu-3\mu)} \cdot \frac{dt}{ds}, \quad (11) \end{aligned}$$

$$\frac{d^2 \theta}{ds^2} - \sin \theta \cdot \cos \theta \cdot \left(\frac{d\phi}{ds} \right)^2 + 2(1/r + \frac{1}{2} \mu') \frac{dr}{ds} \cdot \frac{d\theta}{ds} = 0, \quad (12)$$

$$\frac{d^2 \phi}{ds^2} + 2(1/r + \frac{1}{2} \mu') \cdot \frac{dr}{ds} \cdot \frac{d\phi}{ds} + 2 \cot \theta \cdot \frac{d\phi}{ds} \cdot \frac{d\theta}{ds} = 0, \quad (13)$$

$$\frac{d^2 t}{ds^2} + \nu' \cdot \frac{dr}{ds} \cdot \frac{dt}{ds} = \frac{\epsilon \epsilon'}{4\pi} \cdot \frac{1}{m' c^3 r^2} e^{-\frac{1}{2}(\mu+\nu)} \cdot \frac{dr}{ds}. \quad (14)$$

In the plane $\theta = \frac{\pi}{2}$, (13) becomes

$$\frac{d^2 \phi}{ds^2} + 2(1/r + \frac{1}{2} \mu') \frac{dr}{ds} \cdot \frac{d\phi}{ds} = 0,$$

giving, on integration,

$$r^2 e^\mu \cdot \frac{d\phi}{ds} = \text{constant}. \quad . \quad . \quad . \quad (15)$$

From (11) and (14), eliminating $\epsilon\epsilon'$, we have, after reduction and integration,

$$e^\mu \left(\frac{dr}{ds} \right)^2 + r^2 e^\mu \left(\frac{d\phi}{ds} \right)^2 - c^2 e^\nu \left(\frac{dt}{ds} \right)^2 + 1 = 0. \quad . \quad (16)$$

For a particle initially at rest, we have

$$\frac{dr}{ds} = \frac{d\phi}{ds} = 0.$$

Hence

$$\left(\frac{dt}{ds} \right)^2 = \frac{1}{c^2 e^\nu},$$

and from (11),

$$\frac{d^2 r}{ds^2} + \frac{1}{2} c^2 \nu' e^{\nu-\mu} \left(\frac{dt}{ds} \right)^2 = \frac{\epsilon\epsilon'}{4\pi} \frac{1}{m' c r^2} e^{\frac{1}{2}(\nu-\mu)} \frac{dt}{ds}.$$

From these two last equations, we obtain, neglecting terms with higher negative powers of r than r^{-2} ,

$$m' \frac{d^2 r}{dt^2} = \frac{\epsilon\epsilon'}{4\pi r^2} - \frac{m' p c^2}{r^2},$$

which will be the equation of motion of a particle at great distances from the origin.

We may, then, identify the constant ϵ with the electric charge (in Heaviside units) on the attracting particle, and the constant p with $\frac{km}{c^2}$, where k is the constant of gravitation and m the mass of the attracting particle; for this will give the Newtonian expression for gravitational attraction in the second term on the right-hand side of the equation.

$$q \text{ then becomes } \frac{k}{c^2} \left\{ m^2 k - \frac{\epsilon^2}{4\pi} \right\}.$$

It is easily shown by writing $r=f(r_1)$ in the expression for ds^2 given by Nordström, and solving the differential equation obtained by equating the coefficients of the differentials, that the form for ds^2 obtained in (10) is deduced from that expression by writing

$$f(r_1) = r_1(1 + p/r_1 + q/r_1^2).$$

XXVI. *On the Anomaly of Strong Electrolytes with special Reference to the Theories of J. C. Ghosh.* By HENRY J. S. SAND, D.Sc., Ph.D., F.I.C.; Sir John Cass Technical Institute, London*.

PART II.

Ghosh's Theory of Electrolytic Conduction.

WE now come to the examination of Ghosh's theory of conduction in solutions. The first assumption we have to consider postulates that certain ions are bound, while others, having sufficient kinetic energy, are capable of conducting electricity, or are free to move past each other in the liquid. Since this freedom to move past each other is independent of the current, we must assume that free ions may occupy any position whatever in the liquid. We have already had occasion to refer to the assumption that the ions have a mean disposition in space conforming to regular patterns, and we pointed out that at best these patterns could only be considered "reference arrangements." To obtain a coherent representation of Ghosh's theory of electrolytic conduction it appears to me necessary to assign the following properties to the arrangements of reference. First, the actual arrangement of ions in the solution at any instant is, so far as conduction of the current is concerned, replaceable by that of the reference arrangement, so that to every ion in the actual solution a position in the reference arrangement corresponds. The kinetic energy of an individual ion in the reference arrangement is not in general the same as that in its actual position in the solution, being in some cases greater in others smaller, according to whether its potential energy in the reference arrangement is smaller or greater than in the actual arrangement. The total kinetic energy of translation is, however, in both cases the same, and its distribution in both cases obeys Maxwell's law. Inasmuch as reference arrangements have axes it must be assumed that these may be placed in any arbitrary direction, *e.g.* in that of the applied electric field. Secondly, positions of ions of the same kind in the reference arrangement are interchangeable so far as conduction of the current is concerned, so that, *e.g.* confining ourselves for the moment to binary electrolytes, the work required to remove any one ion from the reference arrangement while all the others are left fixed, has a definite value independent of the ion chosen. This work can readily be

* Communicated by the Author.

calculated to be equal to $2W/\nu$, if W is the work required to separate all the ions completely and ν is their number. The fundamental assumption made by Ghosh is that only those ions "can escape from the field inside the solution" or are "free" whose kinetic energy is greater than G/ν . It will be remembered that the interpretation given by Ghosh to the quantity we have indicated by G is the same as W applied to an original mol; but that we have been compelled to leave the question open whether this interpretation can be justified or not. It may be pointed out here that W/ν and hence possibly G/ν is the work that would have to be done to remove one ion from the system if we could imagine the operation carried out on successive ions in such a way that the amount of work expended on each was the same. This fundamental assumption is in no way supported by proof, and, as mentioned in the introduction, does not lead to Ghosh's final formula (see Chapman and George, *loc. cit.*).

Inasmuch as the transference of electric current through the solution may be considered to consist essentially in the drifting past each other in the direction of the electric field of oppositely charged ions, all transference in directions at right angles to this being ineffective so far as transmission of the current is concerned, we propose to substitute for Ghosh's assumption just referred to, the one: only those ions are "free" whose kinetic energy arising from the velocity component u in the direction of the electric field is greater than G/ν . Indicating the number of ions into which a molecule dissociates by n , so that $\nu = nN$, the condition we have assumed is expressed by saying that only those ions are "free" for which the kinetic energy arising from the velocity-component u is greater than the value

$$K_u = \frac{G}{nN} \quad \dots \dots \dots (22)$$

Another assumption contained in Ghosh's theory is, that the electric field due to other ions has no influence on the mobility of "free" ions. This assumption is probably approximately correct, for it may reasonably be supposed that hindrances to the motion of "free" ions due to the electric field in certain positions are largely balanced by aids in other positions. We now come to an assumption which is an implied one, and which we propose to abandon. It is to the effect, that the contribution of an ion to conductivity is independent of its velocity or that the "mobility" of all ions of a given substance is the same. Owing to the extreme frequency of the collisions that molecules and ions in a liquid

are subject to, what we have called translatory motion will be akin to vibration. Actual translatory motion in a given direction will be extremely slow and will be the result of the frequency with which molecules or ions are capable of slipping past each other in any given direction. This again will depend on frequency of collision and in particular on the velocity-component in the direction considered. In a similar way an externally impressed electric field will be only operative in slightly increasing the probability of ions slipping past each other in its direction. This effect, however, may be supposed to depend on the frequency of collisions the ion is experiencing, and we may reasonably assume it to be proportional to the velocity-component of the ion in the direction of the electric field.

We now proceed to express these hypotheses mathematically. Confining ourselves in the meantime to the consideration of ν ions of one type, the number having a velocity-component in the direction of the electric field between u and $u + du$ is according to Maxwell's theorem :

$$\nu A e^{-\frac{3u^2}{2\bar{c}^2}} du,$$

where $\bar{c}$ is the root mean square velocity of the type considered and A is a constant of known value. According to the hypothesis just proposed, the contribution to the molecular conductivity made by these is

$$d\lambda = \nu \kappa A u e^{-\frac{3u^2}{2\bar{c}^2}} du,$$

where κ is a constant. The contribution to molecular conductivity of the ions having velocity-components between u and infinity is thus :

$$\lambda = \nu \kappa A \int_u^\infty u e^{-\frac{3u^2}{2\bar{c}^2}} du = \nu \kappa A \frac{\bar{c}^2}{3} e^{-\frac{3u^2}{2\bar{c}^2}};$$

so that making $u=0$, we find for the contribution to molecular conductivity of all the ions of the type considered :

$$\lambda_\infty = \nu \kappa A \frac{\bar{c}^2}{3}.$$

For the ratio $\lambda : \lambda_\infty$ we thus have :

$$\frac{\lambda}{\lambda_\infty} = e^{-\frac{3}{2} \frac{u^2}{\bar{c}^2}}.$$

If m is the mass of each ion, K_u the portion of its kinetic

energy arising from the velocity-component u , and N Avogadro's number, we have :

$$\frac{1}{2}mu^2 = K_u \quad \text{and} \quad \frac{1}{2}Nm\bar{c}^2 = \frac{3}{2}RT.$$

Hence, eliminating u and $\bar{c}$ we find :

$$\frac{\lambda}{\lambda_\infty} = e^{-\frac{K_u N}{RT}}.$$

The same formula will hold for the corresponding ratio of any other type of ion and therefore also for the ratio of the molecular conductivities $\mu : \mu_\infty$ arising from the sum of these ions. Expressing K_u in terms of G according to the hypothesis made (equation (22)) we thus obtain :

$$\frac{\mu}{\mu_\infty} = e^{-\frac{G}{nRT}},$$

which is Ghosh's fundamental formula 2, p. 451, *loc. cit.*

We have thus proved that it is possible by a slight alteration of the hypotheses made by Ghosh, to obtain his formula. Moreover, it appears to me that the alterations are inherently defensible and tend to strengthen the theory. On the other hand, we cannot close our eyes to the fact that the number of assumptions which is explicitly and implicitly contained in the original theory gives to the deductions from it the character only of empirical formulæ. Moreover, I have after extended attempts to deduce the subsidiary hypotheses from the fundamental ones come to the conclusion that the former can at best have only approximate validity. Nevertheless it seems to me that the general idea underlying the theory can be defended. It is this, that the small potential-gradients which can be artificially impressed on a solution will, in the case of ions having small kinetic energy, only slightly distort their orbits without leading to effective conduction of the current. Another way of putting this is to say that the current is in the case of the bound ions employed at first in creating kinetic energy which is subsequently annulled by acting in opposition to the current.

*Theories of complete ionization in a uniform dielectric
and Ohm's law.*

We are thus led to the consideration of what seems to me the most serious objection to theories of a completely ionized solute in a medium of uniform dielectric constant. This is, that it appears on such theories that the current should be

employed at first in creating a polarization in the liquid itself, which would later act in opposition to it, and which would be equivalent to a resistance. Hence, the resistance of an electrolytic solution to rapidly alternating currents should be smaller than to continuous current. No such effect has, however, been observed even at very high frequencies*. In fact, it appears that the conductivity should in the first instant when the current is applied have the same value whether internal electric fields exist or not. For, let us consider a thin layer of finite (say, of unit) surface and thickness dx in the electrolyte, taken perpendicularly to the flow of the current, and let the gradient of potential across the layer everywhere be $\frac{dP}{dx}$. If C is the

concentration of electrolyte in the solution, the total amount in this layer, since it may be considered very large in two dimensions relatively to molecular magnitudes, will correspond to the average composition of the solution, *i. e.* it will be equal to Cdx . The distribution of ions in the layer we may, however, suppose to be governed by Boltzmann's theorem, and there will be more ions of negative than of positive potential energy. The total kinetic energy of ions in positions of low or of negative potential energy is thus, according to familiar reasoning, greater than that of ions in positions of high potential energy; but we may assume the distribution of kinetic energy among ions having a given potential energy to conform to Maxwell's law, independently of what that potential energy is. Hence the total distribution of kinetic energy among ions will be the same as it would be in the absence of attraction between them, and if, as we have assumed, the mobility of an ion is proportional to its velocity, the total average mobility in the first instant when the current is applied should likewise be the same whether the ions are in positions where they attract each other or not.

We may consider the matter from another point of view. We may ascribe to ions in positions of negative or low potential energy a higher concentration than to those of high potential energy, so that when the potential gradient $\frac{dP}{dx}$ is first applied for the small time dt , the amount of electricity crossing any small part dA of the surface we are

* See J. J. Dowling and K. M. Preston, *Phil. Mag.* xliii. p. 537 (1922); E. D. Eastman, *J. Amer. Chem. Soc.* xlii. p. 1648 (1920); J. J. Thomson, *Proc. Roy. Soc.* xlv. p. 269 (1880).

considering will be $-kC df \frac{dP}{dx} dt$, where k is a constant, whereas the concentration C varies from point to point. The total amount of electricity crossing unit surface will thus be $(\Sigma C df) \frac{dP}{dx} dt$. The amount of substance contained in the layer of thickness dx and unit surface we have been considering is $\Sigma C df dx$ and is also $C' dx$, C' being the average concentration, so that $\Sigma C df = C'$, and hence the amount of electricity crossing unit surface in the time dt will be $C' \frac{dP}{dx} dt$, independently of the circumstance that the concentration of ions in the layer is not uniform. The theories of Milner, Hertz, and Ghosh dealing with conduction in a completely ionized solution have all aimed at determining the condition in the electrolyte when a permanent state is established, and hence they do not bear upon the effect we have discussed.

Similarly these theories all assume that the distribution of ions in the solution is not affected by the passage of the current, since only on this assumption will conduction obey Ohm's law. Milner nevertheless points out * that the passage of the current will tend to alter the distribution of ions into a random one. Ghosh postulates that his "bound" ions should remain bound, irrespective of the magnitude of the applied potential gradient. In the type of system assumed by Ghosh we should, however, expect a small proportion of bound ions, whose kinetic energy almost suffices to make them free, to become quite free when an external potential gradient was applied. This proportion should vary with the applied potential gradient and should cause a deviation from Ohm's law which should become appreciable for high potential gradients. No such deviation has, however, been observed †.

We are thus led to the conclusion that at every instant in which an ion is "bound," it is bound very much more firmly than would be the case for a completely dissociated electrolyte in a medium of continuous dielectric constant, and that the manner in which it is held must be more analogous to chemical combination. We have, however, already seen that on the assumption of a continuous dielectric constant there are cogent reasons for believing in the practically complete dissociation of electrolytes such as sodium chloride.

* Phil. Mag. xxxv. p. 353 (1918).

† See particularly Taylor and Acree, J. Amer. Chem. Soc. xxxviii. p. 2416 (1916).

We therefore find ourselves compelled to abandon the assumption of a medium of uniform dielectric constant and instead to consider the action of the molecules of solvent as that of discrete particles. A similar position has been reached by Milner proceeding on different lines*, who suggests that the general effect of the action of molecules of solvent as discrete particles "would be to increase the attraction between an ion and the nearest one to it of unlike sign at the expense of the attraction of the more distant ones."

It is doubtful whether the time has yet come for an attempt to give a full theory of conduction in an electrolytic solution, but it may be permissible to point out which considerations, in my opinion, are most likely to lead to a representation agreeing to some extent with experiment. On the basis of present-day theories we must assume the molecules of water and other solvents to contain an equal number of positive and negative charges which, for our present purposes may be considered to be point charges, and it appears to be generally accepted that the molecules of water and other ionizing media have polar properties. By this we mean that charges of one sign are disposed unsymmetrically. The simplest, though by no means adequate, representation of a water molecule will therefore be a simple bipole consisting of one positive and one negative charge rigidly connected like the poles of a magnet. This conception appears to have been introduced into theoretical physics by P. Debye†, who successfully employed it to explain the dielectric properties of the medium. It is obvious that if a medium consisting of such bipoles be placed in an electric field and the bipoles are free to set themselves in it, this would give to the medium the properties of one of very high dielectric constant. However, this is opposed by the rotational energy of the bipoles around axes disposed at right angles to their own axes. Thus, in small electric fields the time during which a bipole is set in the direction of the electric field will be only slightly greater than that during which it is in opposition to it. In very powerful fields, such as those near an ion, the rotation of many of the bipoles will be stopped and converted into vibratory motion around a position of equilibrium, so that we shall have, according to Milner, "surrounding each ion a number of polarized water molecules which tend to form chains linking

* Phil. Mag. xxxv. p. 363 (1918).

† Phys. Zeit. xiii. p. 97 (1912); *Verh. d. D. Phys. Ges.* xv. p. 777 (1913).

together pairs of temporarily nearest oppositely charged ions." Their action would be to a certain extent "analogous to the action of iron filings in forming chains between two magnetic poles." Following up this idea further we may consider each ion in conjunction with one or more water-molecules to be of the nature of a hydrated or complex ion which as a whole would be capable of rotary or vibratory motion. In contrast to the original ion it may very well have polar properties, so that meeting chains of polarized water-molecules in the liquid it might be stopped in its rotation and then, being only capable of vibration around a position of equilibrium, become "bound" or incapable of transmitting current. It is interesting to note that if we have nN isochronous vibrators, the sum of whose energy is nRT , the fraction having a larger energy than $\frac{G}{nN}$ is $e^{-\frac{G}{nRT}}$, which is Ghosh's formula for the fraction of ions that are free in a solution. It may be said to be probable that a further consideration, particularly of the vibrational and rotational energy of molecules of solvent and of solvated ions, will ultimately lead to a satisfactory theory of the anomaly of strong electrolytes.

Test of Ghosh's conductivity formula by experiment.

In testing his formulæ by experimental results Ghosh utilizes in the first instance measurements made on solutions of a concentration of one-tenth to one five-thousandth normal, and later, after the introduction of a viscosity correction, extends his examination to solutions of half normal strength. The formulæ contain the parameter μ_∞ representing the molecular conductivity at infinite dilution which cannot be derived directly from experiment and to which various investigators have attached different values for given electrolytes. Inasmuch as formulæ proposed by other investigators contain more than one parameter, Ghosh's equations may be said to claim a wider generality than any of these. The values utilized for μ_∞ by Ghosh are higher than those hitherto proposed. Thus for KCl, Washburn* quotes the following, proposed by other investigators: 127.9 (Müller & Romain), 128.3 (Kraus & Bray), 128.5 (Wegscheider), 130.0 (Kohlrausch, and Noyes & Falk), to which is added 129.64 contributed by Weiland in Washburn's laboratory.

* J. Amer. Chem. Soc. xi. p. 196 (1918).

Ghosh's value, on the other hand, is 132.2. Since a one-parameter formula requires for its test at least two experimental values of which one may be made to agree with the formula, we may follow Ghosh's procedure in the case of an aqueous solution of potassium chloride and make μ_{100} agree with the experimental value 122.5. We then calculate μ values for the following concentrations, $C_1 = 2 \times 10^{-4}$, $C_2 = 2 \times 10^{-5}$, $C_3 = 10^{-5}$, as follows: $\mu_1 = 129.9$, $\mu_2 = 131.4$, $\mu_3 = 131.7$; whereas the experimental values found for these quantities in the very accurate work of Weiland are $\mu_1 = 129.0$, $\mu_2 = 129.5$, $\mu_3 = 129.6$. Even if we allow for the great experimental difficulties involved in determining μ at the high dilutions quoted and for the fact that the values contain corrections for the conductivity of the water which are perhaps not altogether certain, it appears that Ghosh's calculated values at extreme dilutions are somewhat high relatively to μ_{100} . We therefore abandon the attempt to make the formula fit extreme dilutions and shall confine ourselves to concentration-ranges of about 10^{-1} to 10^{-3} normal. The most direct and searching test to apply to formulæ such as those of Ghosh connecting two entirely different branches of physical inquiry, is to determine the same constant independently from numbers taken first from the one and then from the other branch and compare the values obtained. This was the method employed in testing Ghosh's formulæ for i values. We deduce from Ghosh's equation for univalent binary electrolytes:

$$\frac{\log_{10} \mu_2 - \log_{10} \mu_1}{\sqrt[3]{C_1} - \sqrt[3]{C_2}} = K, \quad \dots \quad (23)$$

where μ_1 and μ_2 are molecular conductivities at the two arbitrary concentrations C_1 and C_2 (mols/litre), and the constant K has the value

$$K = \frac{\log_e 10 F^2}{10 \sqrt[3]{4} \epsilon R T \sqrt[3]{N^2}}, \quad \dots \quad (24)$$

all the terms having the significance used above in equation (18).

Making for 18° ,

$$\epsilon = 81, \quad T = 291, \quad N = 6.16 \times 10^{23}, \quad R = 8.32 \times 10^7,$$

we obtain from equation (24): $K = 0.1615$. With this may be compared the values for K calculated from conductivity measurements on a considerable number of univalent binary

electrolytes, according to equation (23). See Table V. It will be seen that the agreement is very good, allowing for the searching nature of the test. The mean value for K derived from Table V. is 0.1698. It is interesting to note that from this value the number 5.7×10^{23} would be calculated for Avogadro's constant.

TABLE V.

Values of constant K calculated from conductivity measurements according to equation (23) for comparison with $K=0.1615$ following from equation (24).

Salt.	C_1 .	C_2 .	μ_1 .	μ_2 .	K .
KCl	$\begin{cases} 10^{-1} \\ 10^{-1} \end{cases}$	$\begin{cases} 10^{-3} \\ 2 \times 10^{-4} \end{cases}$	$\begin{cases} 112.0 \\ 112.0 \end{cases}$	$\begin{cases} 127.6 \\ 129.1 \end{cases}$	$\begin{cases} 0.1355 \\ 0.1521 \end{cases}$
NaCl	$\begin{cases} 10^{-1} \\ 10^{-1} \end{cases}$	$\begin{cases} 10^{-3} \\ 2 \times 10^{-4} \end{cases}$	$\begin{cases} 92 \\ 92 \end{cases}$	$\begin{cases} 106.5 \\ 107.8 \end{cases}$	$\begin{cases} 0.1746 \\ 0.1697 \end{cases}$
LiCl	10^{-1}	10^{-3}	82.4	96.5	0.1884
CsCl	10^{-1}	10^{-3}	113.6	130.6	0.1663
NH ₄ Cl	10^{-1}	10^{-3}	110.7	127.3	0.1664
KBr	10^{-1}	10^{-3}	114.2	129.4	0.1490
KI	10^{-1}	10^{-3}	113.9	128.2	0.1411
KNO ₃	10^{-1}	10^{-3}	105.0	122.9	0.1877
NaNO ₃	10^{-1}	10^{-3}	87.4	101.8	0.1819
KC ₂ H ₃ O ₂	10^{-1}	10^{-3}	84.0	98.3	0.1875

TABLE VI.

Values of K derived from conductivity measurements in methyl-alcoholic solution for comparison with $K=0.4121$ (equation (24)) and $K'=0.568$.

Salt.	C_1 .	C_2 .	μ_1 .	μ_2 .	K .
NaI	$\frac{1}{3.2}$	$\frac{1}{5.1.2}$	68.8	82.2	0.4068
NaBr	$\frac{1}{3.2}$	$\frac{1}{5.1.2}$	65.8	82.8	0.5253
NaCl	$\frac{1}{3.2}$	$\frac{1}{5.1.2}$	69.6	81.8	0.5611
KI	$\frac{1}{3.2}$	$\frac{1}{5.1.2}$	73.8	91.0	0.4784

For univalent binary electrolytes in methyl-alcoholic solution at 25°, we make $\epsilon=31$, $T=298$, and find from equation (24), $K=0.4121$. Owing to the fact that the attraction for

each other of oppositely charged ions is here 2.613 times as great as in aqueous solution, we should expect the formula for K to be modified in a manner analogous to that proposed by Ghosh for bivalent binary electrolytes. For the latter the attraction of two oppositely charged ions is four times as great as that of two univalent ions under similar circumstances, and Ghosh proposes a distribution of ions which leads to a value of his A and therefore of K , $4\sqrt[3]{4}$ times as great as that for univalent ions. In analogy to this, we should suggest for methyl-alcoholic solutions of univalent ions in which the attraction of two ions for each other is 2.613 times as great as in aqueous solution a value of K , $2.613\sqrt[3]{2.613}$ times as great as it would be in aqueous solution, i.e. in the present instance $K' = 0.568$. With this value we compare that obtained from a number of conductivity measurements which are assembled in Table VI. Here again the agreement may be said to be good.

For salts like BaCl_2 the agreement is not so good. Thus for K the value 0.373 is calculated from Ghosh's formulæ, which may be compared with the values derived from conductivity measurements in Table VII.

TABLE VII.

Values of K for salts like BaCl_2 for comparison with the value $K = 0.373$.

Salt.	C_1 .	C_2 .	μ_1 .	μ_2 .	K .
CaCl_2	10^{-1}	10^{-3}	87.9	111.5	0.2836
SrCl_2	10^{-1}	10^{-3}	90.2	114.5	0.2845
BaCl_2	10^{-1}	10^{-3}	92.2	116.9	0.2831

It may be asked whether Milner's virial values substituted into Ghosh's conductivity formulæ in place of the latter's G values yield better agreement with experiment. This is not the case. In Table VIII. results for the molecular conductivity of potassium chloride calculated according to both formulæ are given. The calculated conductivity at a concentration of $N/100$, at which Milner's and Ghosh's virial values practically agree (see Table I.) has in both cases been made equal to the experimentally found value, and molecular conductivities at other concentrations are calculated from it.

TABLE VIII.

Molecular conductivities of KCl calculated according to Ghosh's formula, using (1) Ghosh's, (2) Milner's virial values. The values for μ_{100} have been made to agree with the observed values.

Concentration...	10^{-1}	5×10^{-2}	10^{-2}	10^{-3}	2×10^{-4}	2×10^{-5}	10^{-5}	0.
μ { observed ...	112.0	115.9	122.5	127.6	129.0*	129.5*	129.6 *	—
calc. with Ghosh's virial ...	111.7	115.7	122.5	127.9	129.9	131.4	131.7	132.7
calc. with Milner's virial ...	104.1	111.7	122.5	129.2	131.1	—	—	132.7

* Weiland's values.

Summary and Conclusions.

1. On the assumption of a uniform dielectric constant of the solvent medium, the view that solutions of electrolytes such as sodium chloride are practically completely dissociated is well founded.

2. Ghosh's formulæ for osmotic pressure and conductivity of solutions must be considered as empirical formulæ. They cover a wide range, but limits have been indicated in several directions.

3. The statement of Ghosh's subsidiary hypotheses has been corrected so as to make them agree with his mathematical formulæ. Although the theory is on the whole strengthened thereby, the number of stated and implied subsidiary hypotheses is so great that the deductions drawn from them cannot be considered essentially different from empirical formulæ.

4. Reasons are given to show that hindrances to conduction arising from the electric fields due to ions in a completely dissociated electrolyte dissolved in a medium of uniform dielectric constant would be of the nature of polarization in the liquid itself. Its conductivity should be greater with rapidly alternating currents and under very high potential gradients than with constant small potential gradients.

5. Owing to the absence of such effects as those mentioned under 4, the idea of a solvent medium of continuous dielectric constant has been abandoned, a conclusion previously reached by Milner on different grounds.

6. The nature of the dielectric properties of the solvent as well as its rôle in determining whether an ion is free or bound at a given instant have been considered and the importance of the rotational and vibrational energy of molecules of solvent and solvated ions has been emphasized.

August 1922.

XXVII. *The Visibility of Individual Spectra.* By F. H. NEWMAN, D.Sc., A.R.C.S., Head of the Physics Department, University College, Exeter*.

[Plate III.]

1. INTRODUCTION.

SPECTROSCOPY furnishes many instances where both the intensity and the nature of the radiations emitted, when an electric discharge is passed through a gas or vapour, depend on the nature of the discharge; argon and the heavier inert gases are the most conspicuous examples. The "red spectrum" of argon is produced by the uncondensed electric discharge, while the condensed discharge develops the "blue spectrum." As the result of mixed conditions a "white spectrum" is sometimes obtained. It is also possible by gradually decreasing the current through the gas to change the colour of the radiation emitted, although the electric force in the tube may remain practically constant. The current density is an important factor in these changes, and it is possible to explain them by considering Bohr's theory of the atom, and the manner in which the atom returns to its normal state after ionization.

The luminosity in an electric discharge-tube does not depend entirely upon the kinetic energy of the moving electrons; for the current, as well as the electric force, affects the brightness, and if the current density is doubled it is found that the intensity of the radiation emitted is more than doubled. The brightness is determined partly by the number of electrons present, for the kinetic energy of the electrons is independent of the current, provided the electric force remains the same.

Although the Lewis-Langmuir theory of atomic structure explains the greatest number of different phenomena, it does not explain the series relation in spectra. The Bohr theory, in conjunction with that put forward by Sommerfeld, of the existence within the atom of a series of non-radiating orbits, any one of which an electron may occupy temporarily, has been found the most satisfactory one; although it accounts for the spectra of hydrogen and helium, it does not explain completely, as yet, the existence of the several series of non-radiating orbits which are necessary to give all the lines of the spectra of elements other than hydrogen and helium.

When an atom is ionized through the inelastic impact of

* Communicated by the Author.

an electron having energy equal to, or greater than, the ionization potential, and recombination takes place, the electron in returning to the orbit which it normally occupies may stop for a short interval at any one of the orbits which are stable, and which are intermediate between the innermost stable orbits and the outside of the atom. As the electron falls from one of these temporary orbits to the next, radiation of that frequency which corresponds to the difference in energy in the two orbits is emitted. Recombination will occur throughout the volume of the gas or vapour, and, as a result, a spectrum consisting of many lines—the number of lines being equal to the number of possible orbits—will be obtained. The question naturally arises whether there is a process during ionization which is the reverse of that occurring during recombination. Does the electron in passing from the atom assume temporarily positions in the stable orbits before it is finally ejected from the atom? If it does, it must proceed by definite steps, and the sum of the energies required for all these steps must equal the ionization potential of the atom. Low voltage arcs in metallic vapours can be explained by this theory. Compton* has suggested that, by the absorption of light, due to the resonance potential, an electron is lifted to one of these stable orbits, and then it requires a smaller amount of kinetic energy from a colliding electron before it is removed completely from the atom. The electron may be raised from the stable orbit to the less stable one by absorption of the corresponding line radiation, or by a colliding electron; and it may be finally ejected from the atom either by absorption of radiant energy, or by the impact of electrons possessing the requisite kinetic energy. Compton states that it is probable ionization is produced at potentials less than the normal ionization potential only in the case of monatomic gases and vapours. This “cumulative ionization” becomes an increasingly important factor in ionization as the ability of any atom to absorb the resonance radiation from neighbouring atoms increases. Then this radiation is passed on from atom to atom, and so the fraction of the atoms which are in the partially ionized state is increased. Complete ionization becomes more general, with the result that the luminosity increases.

The number of atoms in this abnormal state increases as the pressure of the gas becomes greater. The mean free path of the electron is so large at low pressures that it is possible

* Phil. Mag. vol. xliii. (1922).

to develop any required velocity during the interval between successive inelastic impacts. The ionization in this case is due, in the main, to the colliding electrons. When the pressure, and so the number of atoms present, becomes great, with corresponding decrease in the mean free path of the electrons, most of the latter will collide inelastically before the ionization potential energy has been attained, so that the necessary energy must have been acquired partly by the absorption of resonance radiation. At high pressures more radiation will be emitted owing to the greater number of collisions. Increasing the current density will have the same effect.

Considering the discharge of electricity through a mixture of gases or vapours, the relative brightness of the individual spectra is determined by the fraction of atoms ionized. This will depend upon the ionizing potentials, and the actual number of atoms of the components which are present. From what has been stated above, the ionizing potential may be partly acquired by absorption of radiation, so that the current density will be an important factor in the relative luminosity of the spectra, and in the relative brightness of the individual lines in any one spectrum. Argon, for example, has its brightest lines in the less refrangible regions with the uncondensed discharge, while the spectrum developed by the condensed discharge has its brightest lines in the blue. The first line in a principal series is nearly always developed at a lower potential—the resonance potential—than the remaining lines. Owing to the increased energy supplied by the condensed discharge, a greater proportion of the atoms are totally ionized. The electrons in their mean free paths acquire the energy sufficient to ionize the atoms of the gas, with the result that all the lines in the spectrum are developed, whereas with the smaller energy supplied by the uncondensed discharge the electrons only acquire resonance energy and the more refrangible lines in the spectrum are missing. Theoretically, as the energy is increased from the resonance potential to the ionizing potential, successive lines of the spectrum, starting from the less refrangible end, should be emitted. This has actually been observed in the case of mercury vapour by Franck*.

Returning to the case of a mixture of vapours, providing the atoms of the two components are present in equal numbers, that component having the smaller ionizing

* *Zeitschrift für Physik*, xi. (1920).

potential should always emit its spectrum to a greater degree than the other. If, however, the ionizing potential is acquired by "cumulative action" the spectrum will be produced at a potential lower than that normally required, and in this way it is possible for the gas or vapour of the higher ionizing energy to emit the brighter spectrum. Since this effect is greatest at high current densities, such as are obtained with the condensed discharge, if the number of atoms present remain the same, and it is found that the spectrum of the component of greater ionizing potential becomes brighter as the current density is increased, this can be explained by "cumulative action."

In the present work an electric discharge was passed through a mixture of the vapours of an alkali metal and mercury, and keeping the temperature and so the partial pressures constant, the nature of the discharge was varied. It was found that the relative brightness of the individual spectra produced changed considerably as the energy of the discharge was altered.

2. EXPERIMENTS.

A silica vacuum tube fitted with lead seals, and having a capillary portion, was used. The mercury and alkali metal were maintained at $200^{\circ}\text{C}.$ throughout all the experiments by enclosing the tube within an electric heater. The amounts of the metals present were always such that the partial pressures were the maxima at the temperature employed. The tube was evacuated while the amalgam was kept boiling, in order to eliminate any gaseous impurity such as hydrogen, which is freely emitted from the alkali metals during the first stages of the heating and discharge. The amalgam was made the cathode, and the resulting spectra in the capillary portion of the tube were observed, and were photographed by means of a constant deviation type of spectrometer when an uncondensed electric discharge was passed through the vapours, and also when a condensed discharge was employed. The relative brightness of the spectra changed considerably under these conditions, and some of the results are shown in Plate III. When a Wehnelt interrupter was substituted for the mechanical make-and-break on the coil, the results obtained were intermediate to those given with a mechanical make-and-break, and with a condensed discharge.

The lithium lines were bright when the ordinary discharge was used, although not so bright as the mercury lines. The vapour-pressure of the lithium at $200^{\circ}\text{C}.$ is exceedingly

small, and it is surprising that the first principal line 6708 is as bright as shown in the photograph. This line and the other lithium lines were completely suppressed when the condensed discharge was employed. With the uncondensed discharge the sodium D-lines always appeared whatever alkali metal was used. They disappeared when the energy of the discharge was increased. The sodium was present as an impurity.

With sodium amalgam, the induction-coil being operated with the ordinary make-and-break, the D-lines were predominant, the mercury lines being almost entirely suppressed. Several of the doublets of the diffuse and sharp series were observed, but they were very weak compared with the D-lines. The latter were very brilliant, and a very bright yellow radiation was emitted from the capillary portion of the tube. At other parts of the tube the mercury spectrum was visible. Replacing the mechanical make-and-break by a Wehnelt interrupter, the mercury lines appeared, although the sodium radiation was still predominant. With the condensed discharge the mercury spectrum became very bright, and hydrogen lines appeared if the discharge was continued for any length of time, the gas being liberated as an impurity from the sodium. The change from the uncondensed to the condensed discharge intensifies the spectrum of the vapour having the greater ionizing potential. It should be noted that the temperature, and so the partial vapour-pressures, remained the same. The alteration in relative brightness of the two spectra is not due to any increase in the number of mercury atoms. At temperatures above and below 200°C . the D-lines were less bright than when the uncondensed discharge was used. It was possible to run the current intermittently for several hours before the characteristic browning of the silica by the sodium vapour made its appearance. The capillary portion of the tube remained quite clear and unobstructed by any condensed sodium vapour.

It has been shown previously by the author* that it is very difficult to excite the potassium spectrum when this vapour is mixed with others. The present experiments seem to indicate that this was due to the excessive current density employed: with a comparatively small current the potassium spectrum was well developed in the presence of mercury vapour, but no lines showed any great brilliancy, and the mercury spectrum was always the brighter. The principal

* Proc. Phys. Soc. vol. xxxiii. (1921).

doublet 4044, 4047 was the brightest line of the potassium spectrum, but several of the doublets of the sharp and diffuse series were observed. The lines produced were fainter, under all conditions, than those obtained with the other alkali metal vapours. Potassium has a lower ionization potential than lithium and sodium, so that one would expect its spectrum to be as bright as the spectra of these two elements, especially as its vapour-pressure is greater. The fact that it is not suggests that the "cumulative action" is weak in this case, and any ionization which occurs is produced entirely by colliding electrons. Because of the high vapour-pressure of mercury, few of the colliding electrons attain the ionizing energy, and consequently the luminosity of the spectrum is feeble.

The condensed discharge caused the potassium spectrum to disappear entirely, the mercury lines alone being visible.

The rubidium lines were bright when the ordinary discharge was passed through a mixture of the vapour of this metal and mercury. The principal doublet 4202, 4216 was very prominent. These lines became feeble when the Wehnelt interrupter was used, and disappeared with the condensed discharge, the mercury lines becoming brighter. If the pressure of the rubidium vapour was increased by raising the temperature, the blue doublet became faint compared with the lines in the less refrangible parts of the spectrum, and the radiation in the capillary was pink in colour. At low vapour-pressures the blue doublet became very bright compared with the less refrangible lines, and the radiation was blue in colour. The energy acquired by the electrons between successive inelastic collisions is small at high pressures, with the result that the less refrangible lines are bright. At low vapour-pressures, the mean free path is so large that the ionizing potential energy is attained by the colliding electrons, and the atoms are ionized. The result is the development of all the lines in the spectrum.

The vapour from caesium amalgam gave spectrum results similar to those obtained with the rubidium amalgam. The 4555, 4593 doublet was very bright with the uncondensed discharge, became fainter with Wehnelt interrupter, and disappeared altogether with the condensed discharge, the mercury spectrum completely masking the caesium line. At temperatures below 200°C . the brightest caesium lines were in the blue, and the radiation was pale blue in colour, but at temperatures above 200°C . the colour changed to pink, and the less refrangible lines of the spectrum were brighter than

those in the blue. These effects are similar to those obtained with rubidium.

3. DISCUSSION OF RESULTS.

When the vapours of mercury and any one of the alkali metals are present in a discharge-tube, and the partial pressures are maintained constant, the spectrum of the alkali metal is always well developed with the ordinary discharge, but is completely masked by the mercury spectrum when the condensed discharge is used. All the alkali metal vapours have smaller ionization and resonance potentials than mercury vapour, so that although the amount of the latter present is comparatively great, yet the electrons during their mean free paths between successive inelastic collisions are more likely to acquire the energy necessary for ionization of the alkali metal atoms. As a result, the concentration of the luminous sources may be great enough to exhibit the spectrum of the alkali metal. With the condensed discharge, and consequent increase in the electric energy, a greater proportion of the mercury atoms will be ionized, because the colliding electrons will attain greater energy during their mean free paths. The mercury lines become very bright. At the high pressures used, the mean free path is so small that it is improbable that the ionizing energy can be obtained by impact alone, and it is probably acquired partly by absorption of radiation. That the condensed discharge does cause the electrons to attain more energy during their mean free paths, is shown by the production of the enhanced lines in a spectrum by this type of discharge, for Sommerfeld has shown that enhanced spectra arise from the removal of more than one electron from the normal atom. Under the conditions of the ordinary electric discharge, it is unlikely that an electron in its path will attain sufficient energy for the removal of two electrons. Some of the electrons may be accelerated, without collision, for several mean free paths, far enough to accumulate velocity sufficient to produce the second type of ionization, but the probability of this happening will decrease with rise of pressure. The energy of the colliding electrons does increase with the condensed discharge, and this accounts for the development of the spectrum of those atoms which have the higher ionization potential.

XXVIII. *A Derivation of Planck's Law of Radiation by means of the Adiabatic Hypothesis.* By JAKOB KUNZ, Associate Professor of Physics, University of Illinois*.

WE change the state of a mechanical or electromagnetic system, which is quantified, infinitely slowly by introducing gradually an external field of force or by changing the masses or charges of the particles. A new state of motion will result which is again quantified. This is the adiabatic hypothesis, which has been studied specially by P. Ehrenfest†. Quantities which remain unchanged in adiabatic processes are called adiabatic invariants. It has been shown that such an invariant is the average kinetic energy E_k of a harmonic oscillator divided by the frequency ν . $\frac{\bar{E}_k}{\nu} = \text{constant}$, an equation which holds also for conditionally periodic motions. If the potential energy is proportional to the kinetic energy, we can write

$$\frac{\bar{U}}{\nu} = \text{constant},$$

where $\bar{U}$ is the total average energy of the oscillator. If the temperature radiation is compressed adiabatically in a perfectly reflecting cavity, then we have also for each principal mode of vibration in the cavity:

$$\frac{\bar{U}_s}{\nu_s} = \text{constant}. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This relation is important in the thermodynamic derivation of Wien's law. Moreover, black radiation remains black radiation by adiabatic compression‡. We shall apply this adiabatic theorem in order to derive Planck's law of radiation in a very simple way.

We shall at first calculate the average energy U of molecules or oscillations in an enclosure of constant temperature T . The number of oscillations, dn , whose energy lies in the interval between U and $U + dU$ is by Maxwell-Boltzmann's law given by

$$dn = C e^{-\frac{U}{kT}} dU. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

* Communicated by the Author.

† P. Ehrenfest, *Ann. der Physik*, li. p. 327 (1916); *Proc. Amsterdam*, xvi. p. 591 (1914). See also A. Sommerfeld, 'Atombau und Spectrallinien,' 3rd edit. p. 374 (1922).

‡ Planck, 'Wärmestrahlung,' 2nd edit. Sect. 71.

The total number of oscillations per unit volume shall be N .

$$N = C \int_0^{\infty} e^{-\frac{U}{kT}} dU. \quad \dots \quad (3)$$

Dividing equation (2) by equation (3) we obtain

$$\frac{dn}{N} = \frac{e^{-\frac{U}{kT}} dU}{\int_0^{\infty} e^{-\frac{U}{kT}} dU}. \quad \dots \quad (4)$$

This form of Maxwell-Boltzmann's law we shall modify by the assumption that an oscillator changes its energy not in a continuous way by dU but in an abrupt way by $\mathcal{E}$, where $\mathcal{E}$ is the quantum of energy. In the cavity we find a number of oscillations each with energy 0, another number with energy $\mathcal{E}$, another number with energy $2\mathcal{E}$, a number n_s of oscillations each with an energy $s\mathcal{E}$, where s is the quantum number. Equation (4) assumes now the form (5) :

$$\frac{n_s}{N} = \frac{e^{-\frac{s\mathcal{E}}{kT}} \mathcal{E}}{\sum_{s=0}^{\infty} e^{-\frac{s\mathcal{E}}{kT}} \mathcal{E}} = e^{-\frac{s\mathcal{E}}{kT}} (1 - e^{-\frac{\mathcal{E}}{kT}}). \quad \dots \quad (5)$$

The energy of these oscillations is equal to $U = n_s s\mathcal{E}$, and the average energy of an oscillation is equal to

$$\bar{U} = \frac{\sum U}{N} = \sum_{s=0}^{\infty} s \mathcal{E} e^{-\frac{s\mathcal{E}}{kT}} (1 - e^{-\frac{\mathcal{E}}{kT}}), \quad \dots \quad (6)$$

$$\bar{U} = \frac{\mathcal{E}}{e^{\frac{\mathcal{E}}{kT}} - 1}. \quad \dots \quad (7)$$

Now we consider an adiabatic compression of the black body radiation in the enclosure. Before the compression we had :

$$\left(\frac{n_s}{N}\right)_1 = e^{-\frac{s\mathcal{E}}{kT}} (1 - e^{-\frac{\mathcal{E}}{kT}}). \quad \dots \quad (5)$$

Through the compression we change the temperature from T to T' and the energy $\mathcal{E}$ into $\mathcal{E}'$; the quantum numbers remain constant. After the compression we have

$$\left(\frac{n_s}{N}\right)_2 = e^{-\frac{s\mathcal{E}'}{kT'}} (1 - e^{-\frac{\mathcal{E}'}{kT'}}).$$

But the character of the relation remains unchanged ;
hence

$$\left(\frac{n_s}{\bar{N}}\right)_1 = \left(\frac{n_s}{\bar{N}}\right)_2;$$

this equation is satisfied if

$$\frac{\mathcal{E}}{T'} = \frac{\mathcal{E}'}{T}.$$

Before the compression the average energy $\bar{U}$ was given by

$$\bar{U} = \frac{\mathcal{E}}{e^{kT}-1}. \quad \dots \quad (7)$$

After the compression we have

$$\begin{aligned} U' &= \frac{\mathcal{E}}{e^{kT'}-1} = \frac{\mathcal{E}'}{e^{kT}-1}, \\ \frac{\bar{U}}{U'} &= \frac{\mathcal{E}}{\mathcal{E}'}; \quad \dots \quad (8) \end{aligned}$$

but from equation (1) we obtain

$$\frac{\bar{U}}{U'} = \frac{\nu}{\nu'}.$$

Hence

$$\frac{\mathcal{E}}{\mathcal{E}'} = \frac{\nu}{\nu'}, \quad \text{or} \quad \mathcal{E} = h\nu, \quad \dots \quad (9)$$

which is the quantum relation of Planck. The average energy $\bar{U}$ becomes now equal to

$$\bar{U} = \frac{h\nu}{e^{kT}-1}. \quad \dots \quad (10)$$

Rayleigh and Jeans have shown that the number of oscillations do per unit volume in the frequency interval between ν and $\nu + d\nu$ is equal to

$$do = \frac{8\pi\nu^2 d\nu}{c^3}. \quad \dots \quad (11)$$

Hence the energy dE in the same frequency interval is equal to

$$\left. \begin{aligned} dE &= d\omega U = \frac{8\pi h\nu^3 d\nu}{c^3(e^{h\nu/kT} - 1)}, \\ \nu &= \frac{c}{\lambda}; \end{aligned} \right\} \dots (12)$$

hence

$$\frac{dE}{d\lambda} = \frac{8\pi hc}{\lambda^5(e^{hc/k\lambda T} - 1)}.$$

This is Planck's law of radiation.

In an oscillation taken at random, we find $f(\nu)$ quanta of energy $\mathcal{E}$; therefore

$$dE = \frac{8\pi\nu^2 d\nu}{c^3} h\nu f(\nu). \dots (13)$$

Comparing (13) with (12) we get

$$f(\nu) = \frac{\lambda}{h\nu} \frac{1}{e^{h\nu/kT} - 1}.$$

Laboratory of Physics,
University of Illinois,
October 10, 1922.

XXIX. *Electrolysis with a Dropping Mercury Cathode.*

Part I. Deposition of Alkali and Alkaline Earth Metals.

By JAROSLAV HEYROVSKÝ, D.Sc., Ph.D., Assistant Professor in Physical Chemistry, Charles' University, Prague*.

INTRODUCTION.

B. KUČERA (*Drud. Ann.* vol. xi. p. 529, 1903) showed that the change of surface-tension of polarized mercury, i.e., the "Electrocapillary parabola," can be very exactly determined by drop-weight. In this method, mercury dropping slowly from a glass capillary in an aqueous solution is polarized, the other electrode being the layer of mercury covering the bottom of the vessel.

In using the dropping mercury as cathode, it has been observed that in neutral or alkaline solutions hydrogen is not evolved even at high polarizations. This arrangement seemed thus convenient to study the cathodic deposition of the most "positive" metals, which are otherwise attacked by water. Besides the high over-voltage the dropping mercury electrode possesses other advantages: it yields in

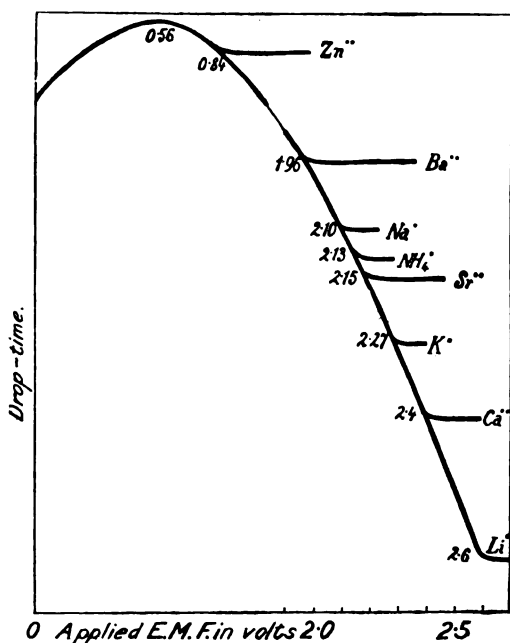
* Communicated by Prof. W. C. McC. Lewis.

the solution always a fresh and pure mercury surface, avoiding thus any "concentration polarization"; further the drops when falling on the bottom mercury used as anode also produce stirring there.

The bottom layer of resting mercury when in a solution of a halide or hydroxide keeps up the well-defined potential of the respective standard electrode, and thus can be relied upon as an exact reference electrode.

With such an arrangement even calcium and magnesium can be deposited in mercury before hydrogen and their amalgam formation can be followed in an exact manner.

Fig. 1.



The ease with which various metals are cathodically deposited in mercury can be determined by observing in each case the shape of the electrocapillary parabola, obtained by the drop-weight method, when readings are continued until considerable amalgam formation is reached. From this point any further increase of polarization does not effect any change in the drop-weight or drop-time. Consequently, when amalgam formation begins, the descending branch of the parabola turns horizontal.

The graph in fig. 1, which refers to decinormal solutions

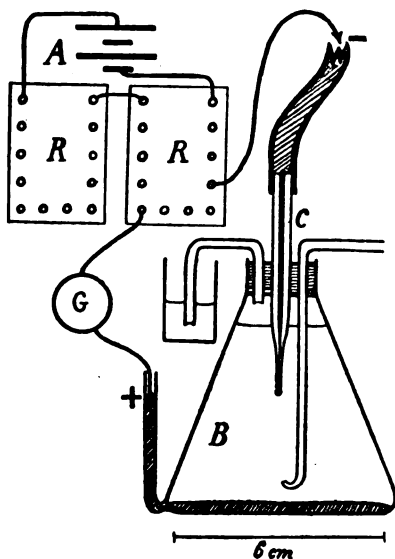
of chlorides of the respective ions, gives us only approximate numbers; the results vary slightly, depending on factors which determine the current, *i.e.*, the size and velocity of drops, strength of the solution, and dimensions of the vessel.

A much more accurate method, however, is to determine in such cases the increase of current caused by the increase of the polarizing E.M.F.; these investigations are described in the following part*.

MEASUREMENT OF THE CURRENT.

The arrangement is shown in fig. 2.

Fig. 2.



The Apparatus. A double lead accumulator A was circulated through two resistance boxes, R. From one of these the current was branched to the electrolysing vessel, which consisted of a conical flask, B, with a platinum contact attached to the bottom; a thick-walled glass capillary passed through the cork stopper C, connected by a rubber tube to a

* See also J. Heyrovský, *Chemické Listy*, vol. xvi. p. 256 (1922).
Phil. Mag. S. 6. Vol. 45. No. 266. Feb. 1923. X

mercury reservoir (not shown in the sketch), by the level of which the rate of dropping could be regulated. The glass tubes, which passed through the stopper, served to lead the hydrogen in and out. The negative terminal of the resistance-box was connected to the mercury reservoir above the capillary, the other was connected through a sensitive galvanometer to the bottom mercury layer in the flask.

The capillaries were drawn out of a thick-walled thermometer capillary, with about 1 mm. inner diameter; they were broken off under water when connected with the mercury reservoir, so that the pure and dry mercury rushed into the tip first. It is essential to have the inside of the tube quite free from dust—however, the capillaries must not be washed nor moistened; for this reason capillaries made of fresh glass have to be used. The break of the tip was chosen so as to yield drops of about 4 to 6 seconds time (*i. e.*, 0.02–0.05 mm. inner diameter of the opening).

Since on prolonged use the capillaries get stopped and moistened inside, which might lead to hydrogen evolution in the tip, they have to be frequently exchanged for new ones.

The reflecting galvanometer of the Kelvin type with an astatic needle had 50 ohms resistance; one millimetre deflexion of scale, when two metres apart from the mirror, corresponded to 10^{-8} ampere.

The Method of Procedure. Before starting polarization, the resistances of the boxes were adjusted so as to be one ohm per millivolt of the E.M.F. of the source (about 4 volts); this E.M.F. was determined by compensation with a standard Weston cell with an accuracy to a tenth of a millivolt and was frequently checked. The vessel was then filled with a solution prepared from Kahlbaum's or Merck's purest specimens, and the stopper was sealed with paraffin-wax. In order to prevent oxidation by air at the cathode, it has been found necessary to pass hydrogen for 30 to 40 minutes through the solution.

The room temperature was kept as close as possible to 20°C .; the maximal deviation $\pm 1^{\circ}$ had no noticeable effect, which probably lies within the experimental errors of the method.

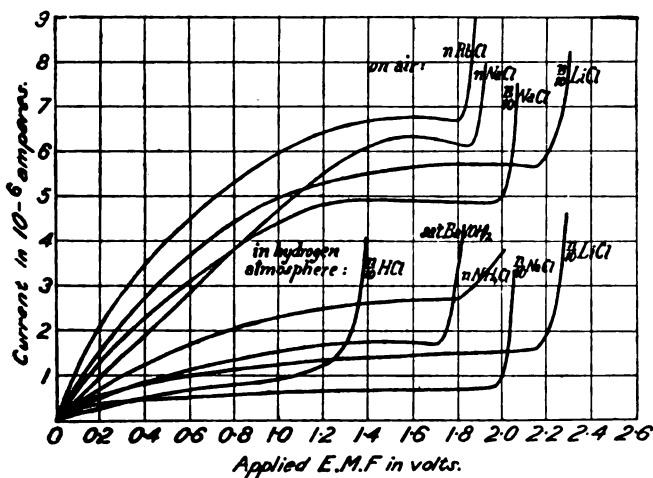
The zero reading of the galvanometer was then taken and the polarization was gradually increased, and for each value of the applied E.M.F. the corresponding galvanometer reading was noted.

OBSERVATIONS.

Some of the typical curves, showing the relation between E.M.F. of polarization and the resulting current, are drawn on the diagram (fig. 3).

When working with solutions in an open beaker in air a small current passes even at small polarizations, which is largely due to oxygen dissolved in solution. The readings in such cases were not steady, but oscillated within sharp limits (1-2 scale divisions) synchronously with the drop-time, this being no doubt caused by the different rates of oxidation of the rhythmically changeable drop-surface. By

Fig. 3.



expelling air with hydrogen, the current was considerably diminished and oscillation stopped entirely.

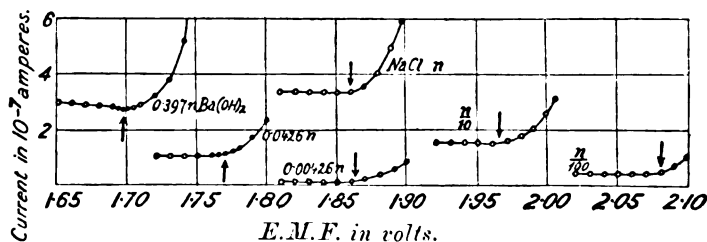
With increasing polarization the current increases at first very slowly until a certain value of the E.M.F. is applied, above which the current increases rapidly, so that a further increase of a few centivolts puts the mirror off the scale. This critical E.M.F. is quite independent of the dimensions of the electrodes of the drop-time and of the amount of air in solution--in fact, it is found to depend only on concentration of the cation.

The independence of the critical polarization, which might be termed the "decomposition E.M.F.," since at this point

extensive electrolysis of the salt sets in, has been ascertained in a series of solutions using different capillaries, with different drop-times (from 1 to 5 secs.), with varying distances between the electrodes (0.5 to 6 cms.) and varying size of bottom layer (from 9 to 60 cm.²), further, with varying external resistance in the boxes (from 0.1 to 10 ohms per millivolt). For very quick drops (less than one sec.) a slight shift towards greater polarizations can be observed; for drop-times greater than 1.5 sec. the results coincided. The slower the dropping, the more steady the galvanometer was; therefore, very narrow capillary openings were used, giving about 3 secs. drop-time at the decomposition polarization.

The decomposition E.M.F. was fixed as the value from which the current begins to increase distinctly in a geometrical progression. Owing to this steep increase it was possible to fix this point in most of the solutions within 2–4 millivolts, in some cases even to a greater accuracy. For this purpose the E.M.F. near this value was increased by 5 millivolts and the exact point found from a graph.

Fig. 4.



The more dilute solutions require larger decomposition E.M.F. (see fig. 4), the differences for a ten-fold dilution of a uni-univalent salt amounting to 110 millivolts, for a bi-univalent salt it is about 80 millivolts, which is the well-known difference of "free energies" at these dilutions (*cf.* McInnes and Parker, *Journ. Amer. Chem. Soc.* 37, p. 1445, 1915). Solutions prepared (by weight or dilution) at different times and from different sources always led to the same decomposition E.M.F.

Traces of noble metals or oxidizing matter in solution cause disturbances in readings; these become troublesome in very concentrated solutions, which therefore had to be

prepared in a high degree of purity to give satisfactory results. For much help in this way the author is obliged to Professor B. Brauner, who presented some of his rare specimens and provided for exact standard solutions.

When a cathode of very small dimensions is polarized, the large reference electrode being used as anode, the decomposition E.M.F. must be equal to the difference between the potential of the electrode used as anode and the potential at which decomposition takes place at the cathode. Let us denote the latter as the "deposition potential" of the cation in mercury. To show that this deposition potential is independent of the anion, solutions of chlorides and hydroxides of the same metal in various dilutions were electrolysed, and from the results the deposition potentials referred to the normal calomel electrode were calculated. For this purpose the exact potential difference of the bottom reference electrode in the vessel from that of the normal calomel electrode had to be determined. Therefore, for most of the solutions a calomel or mercuric-oxide-electrode has been set up and compared with the standard calomel electrode. The potential of these single electrodes never differed by more than two millivolts from the polarized bottom mercury layer when both were in the same solution.

To eliminate the liquid junction potential between the normal electrode and the various solutions, a quarter-saturated, half-saturated, and fully saturated potassium chloride solution has been used and the values extrapolated.

The results are given in Tables I. and II.

The results show distinctly that the polarization at which electrolysis starts, E , depends only on the concentration of the cation being equal to the difference of potential of the resting mercury and the deposition potential of the cation ($\pi_0 - \pi'$).

The value π_x , which is the deposition potential of the cation from a solution containing one gram-ion per litre, has been obtained from π' actually observed at different dilutions by subtracting the free energy of dilution of the ions; here the average numbers observed in concentration cells at room-temperature were used, viz. :—

For ten-fold dilution of uni-valent cations 0.056 volt.

For 100-fold dilution 0.114 volt (known from silver- or hydrogen-ion concentration electrodes).

For bivalent 0.026 and 0.054 volt respectively (from Zn^{++} , Hg^{++} , Ba^{++} concentration cells).

TABLE I.

Deposition of the Alkali Metals, $t = 20^{\circ}\text{C}$.

Solution.	E the observed decomposition E.M.F.	π_0 observed P.D. of the bottom layer from N. cal.	$\pi' = \pi_0 - E$ the deposition potential of the cation.	π_N the calculated normal deposition potential.
n LiCl.	2.05	*0.00	-2.05	-2.05
$\frac{n}{10}$ "	2.16	+0.052	-2.11	-2.05
$\frac{n}{20}$ "	2.22	+0.068	-2.15	-2.07
0.0382 n "	2.26	+0.085	-2.17	-2.07
1.122 n LiOH ...	1.867	-0.1552	-2.022	-2.025
0.108 n " ...	1.960	-0.1138	-2.074	-2.021
n NaCl	1.860	+0.0010	-1.860	-1.860
$\frac{n}{10}$ "	1.968	+0.0521	-1.916	-1.860
$\frac{n}{100}$ "	2.080	+0.1072	-1.973	-1.859
1.076 NaOH.....	1.700	-0.1598	-1.860	-1.862
$\frac{n}{10}$ "	1.810	*-0.104	-1.914	-1.858
$\frac{n}{100}$ "	1.925	*-0.048	-1.973	-1.859
n KCl	1.883	0.000	-1.883	-1.883
$\frac{n}{10}$ "	1.990	0.0532	-1.937	-1.881
$\frac{n}{100}$ "	2.108	0.1080	-2.000	-1.886
n RbCl	1.795	*0.0	-1.795	-1.795
$\frac{n}{10}$ "	1.905	*0.053	-1.852	-1.796
$\frac{n}{100}$ "	2.020	*0.108	-1.912	-1.798
$\frac{n}{10}$ CsCl	1.948	*0.053	-1.895	-1.839
$\frac{n}{100}$ "	2.055	0.1077	-1.947	-1.833
n NH ₄ Cl	1.795	+0.004	-1.791	-1.787
$\frac{n}{10}$ "	1.900	+0.056	-1.844	-1.788
$\frac{n}{100}$ "	2.010	+0.110	-1.900	-1.786

* Values not actually observed, but taken from analogous cases.

TABLE II.

Deposition of the Alkaline-earth Metals, $t=20^{\circ}\text{C}$.

Solution.	E observed.	π_0 observed.	$\pi' = \pi_0 - E$.	π_N calculated.
$m\text{MgCl}_2$	1.890	* -0.011	-1.901	-1.901
$\frac{m}{10}$ "	1.970	* +0.039	-1.931	-1.905
$\frac{m}{10}\text{CaCl}_2$	2.090	* +0.039	-2.051	-2.025
$\frac{m}{100}$ "	2.170	* +0.095	-2.075	-2.021
0.0455n $\text{Ca}(\text{OH})_2$	1.985	-0.0880	-2.073	-2.024
$m\text{SrCl}_2$	1.850	* -0.011	-1.861	-1.861
$\frac{m}{10}$ "	1.930	* +0.029	-1.891	-1.865
$\frac{m}{100}$ "	2.010	* +0.095	-1.915	-1.861
0.119n $\text{Sr}(\text{OH})_2$	1.782	-0.1140	-1.896	-1.862
0.0120n "	1.857	-0.0627	-1.920	-1.860
$m\text{BaCl}_2$	1.800	-0.011	-1.811	-1.811
" "	1.828	+0.004	-1.824	-1.816
$\frac{n}{10}$ "	1.911	+0.0567	-1.854	-1.822
$\frac{n}{100}$ "	1.981	+0.1088	-1.872	-1.810
0.397n $\text{Ba}(\text{OH})_2$	1.699	-0.1337	-1.833	-1.815
0.0426n "	1.770	-0.0875	-1.858	-1.813
0.00426n "	1.862	-0.0363	-1.898	-1.826

The series of the deposition potentials runs as follows :—

Li	-2.023 volts.	NH_4	-1.787 volts.
K	-1.883 "	Ca	-2.023 "
Na	-1.860 "	Mg	-1.903 "
Cs	-1.837 "	Sr	-1.862 "
Rb	-1.796 "	Ba	-1.814 "

Salts of lithium and calcium, owing to their high cathodic deposition, offered difficulties, since traces of other alkalies or alkaline earths present as impurities are deposited first. Moreover, at such great polarizations in quickly dropping capillaries, especially when long in use, bubbles of hydrogen

are evolved. This was still worse with beryllium salt solutions, which, owing to hydrolysis, did not lead to any satisfactory result. Traces of acidity change the electrolysis of salts to that of hydrochloric acid (see in fig. 3) and then hydrogen is evolved before the metal is deposited.

On the other hand, traces of alkalis stabilise greatly the over-voltage and thus remove fluctuations in readings; the alkalinity, however, changes the potential of the resting mercury, making it more negative, and this change has to be measured and taken into account.

The most suitable for these measurements of polarization are alkaline solutions of hydroxides, not only on account of the scarcity of hydrogen ions, but also that the product formed at the anode is mercuric oxide, which is at the same time the depolarizer used in this electrode. Of all solutions, those of baryta are most favourable, as in this instance the traces of all other positive metals would be deposited at much more negative potentials, and impurities of nobler metals are excluded owing to the alkalinity of the solutions.

Electrolysis of dilute ammonium chloride offered no difficulties; it differs from the deposition of metals in that the current curve does not increase so steeply with increasing polarization (see fig. 3). The same was observed with magnesium salts and in concentrated solutions of calcium, strontium, and lithium.

In dilutions greater than hundredth normal the readings became indistinct, in very concentrated solutions impurities mattered much; in concentrated chlorides, moreover, the formation of complexes with mercury brings it in solution, which causes great increase and oscillations of the current. For a similar reason sulphates cannot be used, since mercurous sulphate is considerably soluble and the solution shows increasing conductance during polarization.

DISCUSSION OF THE RESULTS.

There is no doubt that the sudden change in slope of the current-E.M.F. curve (figs. 3 and 4) is due to amalgam formation at the cathode. The formation of amalgams from electrolysis of salts was studied by Coehn and Kettembeil (1901-4), who used aqueous solutions of calcium, strontium, and barium with a mercury cup as cathode. With such an arrangement, however, extensive hydrogen evolution, besides concentration polarization, excludes satisfactory results. Experiments with resting mercury used as cathode repeated by the present author gave the break at much lower and

very changeable potentials, due only to the evolution of hydrogen, which depends on catalytically acting impurities present in solution.

According to the theory of electrolysis, even the slightest polarization, say 0.1 volt, deposits some cations on to the surface of the mercury drop, and forms there an extremely dilute amalgam. A very minute current equivalent to this deposition must pass through the solution, but, since the drop-surface possesses now a more negative potential, the current is stopped by the opposing E.M.F. In increasing the polarizing E.M.F. we increase the minute amalgam concentration in the drop surface and diffusion into the inside must result. The amount which diffuses will be proportional to the concentration of the amalgam in the surface, which is given by the formula

$$\pi = - \frac{RT}{nF} \log K_{Me} \cdot C_{Me},$$

where C_{Me} denotes the amalgam concentration and π the potential of the polarized drop. Thus the current

$$i = k \cdot C_{Me} = K \cdot e^{-\frac{\pi n F}{RT}};$$

i. e. the curve should be an exponential.

It will be noted that the increase of current above the decomposition potential proceeds in a geometrical progression, the curve resembling a steep exponential.

The concentration of the amalgam in the drop-surface at the deposition potential can be estimated from the investigations of G. N. Lewis and his co-workers (1912-15) on the alkali-metal amalgam potentials. Assuming that ten-fold dilution of the extremely dilute amalgam lowers its potential by 0.06 volt, we obtain from the available data a concentration of the order 10^{-6} gram atoms of alkali metals per litre of mercury, *i. e.*, about one millionth of one per cent.

Mercury Drop Potentials. An attempt was made to measure the potential of polarized mercury by placing under the dropping capillary in the electrolysing flask B (fig. 2) a glass cup with a platinum contact. Normal and tenth-normal sodium chloride solutions were used; the potential of the drops collected in the cup was measured against the bottom mercury, or, which was found always to be identical, against a normal or deci-normal calomel electrode connected with the solution. From the beginning of the polarization

and also at the decomposition E.M.F. the drops showed no difference against the pure resting bottom mercury ; however, 40 to 60 millivolts above the decomposition potential the drops in the cup showed already 2 millivolts difference from pure mercury, and this difference increased rapidly, so that at a polarization of 2.10 volts the mercury in the cup was already negative by nearly 2 volts more than the reference electrode. Obviously the most dilute amalgams which are formed at the deposition potential are only superficially polarized and lose their negative potential during the fall, being instantly acted upon by water.

Affinity for Mercury. It is assumed that the positive metals combine with mercury and their compounds are rich in mercury. Recently Richards and Conant (J. Amer. Chem. Soc. xlv. (1922) p. 601) pointed out that even at very great dilutions amalgams do not behave as ideal solutions, showing a rather large decrease in potential and a considerable heat of dilution. The explanation is that even at such dilutions combination with mercury still proceeds.

Supposing complete saturation will once be reached, in an enormously dilute amalgam, as is probably the case in the surface of slightly polarized mercury, we cannot expect that this enormously dilute amalgam will have a tendency to diffuse inside the drop as the particles are lighter than mercury and are completely "solvated" with mercury. As soon as the the amalgam concentration increases so far that it will not allow all atoms to be fully solvated with mercury, affinity for mercury as well as the increased concentration will cause diffusion into the interior of the drops ; from this point the current curve will proceed much steeper than ordinary diffusion could effect, and this probably happens at the deposition potential.

The atoms of the alkali metals in the surface of mercury are under two opposing forces ; the affinity for mercury draws them into the surface, their solution tension, on the other hand, sends them into solution. Thus the deposition potential depends both on the affinity of the metal for mercury and its electrolytic potential. Since at the deposition potential all alkali metals are in an analogous condition, we can use these values to express the relative affinities of the alkali metals for mercury. The deposition potential indicates thermodynamically the very small partial pressure the alkali metal has in the drop-surface ; the combination with mercury has lowered the activity of the alkali metal, indicated by its electrolytic potential (E.P.) to the characteristic value π_N .

Thus the affinity, A , of the metal for mercury is equal to $\pi_N - E.P.$

From the work of G. N. Lewis, mentioned above, and the values π_N we have:—

Metal.	E.P.	π_N .	$A = \pi_N - E.P.$
Li.....	-3.304	-2.023	1.281
Na	-2.998	-1.860	1.138
K	-3.208	-1.883	1.325
Rb	-3.205	-1.796	1.409
Cs	(-3.3)	-1.837	(1.5)

The affinity is expressed in volt-laradays per gram-atom. This series shows that the affinity for mercury increases with increasing atomic weight. Sodium has an anomalous position (*cf.* McPhail Smith, *Zeitsch. Anorg. Chem.* lviii. (1908) p. 381) and behaves like a nobler metal, its amalgam being very stable—in fact, hydrogen was never observed in these experiments to be formed on mercury drops on electrolysis of sodium solutions. Finally, it may be pointed out that the affinity of caesium for mercury, which from extrapolation would amount to 1.5 volt, points to the E.P. of caesium being -3.3 volt (from the calomel electrode).

Besides to Prof. Brauner, the author's thanks are also due to Professors J. Štěrba-Böhm and F. Závíska for their help.

The author wishes to express his indebtedness to the prematurely deceased Professor B. Kučera, who suggested to him the study of the polarization of dropping mercury.

Chemical Laboratory of
the Charles' University,
Prague.

XXX. Indian Drums.

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN India, like kettledrums, there are many drums which are musical, and which are used in company with stringed instruments. They differ from kettledrums in two respects: (1) they are loaded over a central zone, and (2) they elicit harmonic partials ('Nature,' Jan. 15, 1920, p. 500). It is well known that the partials of an unloaded membrane do not form an harmonic series, and a few of them give a consonant chord. From a look at the Indian instruments, it at once becomes evident that the load per unit area varies as

we proceed outwards from the centre. The investigation of the nature of vibration when the load varies inversely (1) as the first power and (2) as the second power of the distance from the centre, can be very simply effected, but the writer could not find any mention in the text-books.

The equation of motion is given by

$$\rho \frac{d^2 w}{dt^2} = T_1 \left\{ \frac{d^2 w}{dr^2} + \frac{1}{r} \frac{dw}{dr} + \frac{1}{r^2} \frac{d^2 w}{d\theta^2} \right\}.$$

Assume $w \propto \cos ket$:

$$\text{Case (1) } \rho = \frac{\rho_0}{r} \quad \text{and} \quad \frac{T_1}{\rho_0} = c^2, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and further assume $w = v \cos n\theta$, then v must satisfy

$$\frac{d^2 v}{dr^2} + \frac{1}{r} \frac{dv}{dr} + \left(\frac{K^2}{r} - \frac{n^2}{r^2} \right) v = 0. \quad . \quad . \quad . \quad (2)$$

Put $x = 2K \sqrt{r}$, then (2) becomes

$$\frac{d^2 v}{dx^2} + \frac{1}{x} \frac{dv}{dx} + \left(1 - \frac{(2n)^2}{x^2} \right) v = 0; \quad . \quad . \quad . \quad (3)$$

$$\therefore \quad v = A J_{2n}(x) = A J_{2n}(2K \sqrt{r}).$$

If at $r=a$ the membrane is fixed, we must have

$$J_{2n}(2K \sqrt{a}) = 0,$$

giving real values of K . The nature of these roots is well known; they do not form an harmonic series. The effect of the variable density is mainly upon the absolute pitch of the membrane.

$$\text{Case (2) } \rho = \rho_0 / r^2. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Let us consider the simple case of symmetrical vibrations only, so that (2) becomes

$$\frac{d^2 v}{dr^2} + \frac{1}{r} \frac{dv}{dr} + \frac{K^2 v}{r^2} = 0; \quad . \quad . \quad . \quad . \quad (5)$$

$$\therefore \quad v = B \cos (K \log r). \quad . \quad . \quad . \quad . \quad (6)$$

The boundary condition gives $\cos (K \log a) = 0$;

$$\therefore \quad K \log a = (2n+1) \frac{\pi}{2}.$$

The partials now form a series of odd harmonics, and the absolute pitch is also disturbed.

R. N. GHOSH.

Muir Central College,
Allahabad, India,
3rd Jan., 1922.

XXXI. *Magnetic Valency and the Radiation Hypothesis.*

By F. T. PEIRCE, B.Sc., A.Inst.P.*

MUCH criticism and fresh experimental data have necessitated large modifications on the original simple views of the radiation hypothesis of chemical reaction, such as those advanced by Perrin in his very comprehensive treatment (*Ann. de Phys.* 9, xi. pp. 1-108). The broad synthesis which it gives seems to inhere in some principle of atomic structure, not necessarily dependent upon radiation.

Some serious objections may be avoided and fertile modifications suggested if we inquire into the possible mechanism which might give a peculiarly effective rôle to radiation of definite frequency. This could hardly be expected of a general electrostatic attraction between atoms. There seems no reason why the forces of a collision should not be as efficacious, or more so, in breaking such a bond, nor why the "activation" of a molecule by a change in an electronic orbit should be necessary for its formation.

The frequencies involved in most reactions are much higher than those of the atoms as a whole, and the supposition of their unique rôle is probable only for a local bond between individual electrons. Such an arrangement, suggested by magnetic phenomena, has been pictured by A. E. Oxley (*Proc. Roy. Soc. A* 98, p. 264, 1921) and is shown diagrammatically in fig. 1. This view of the valency bond is very successful in stereo-chemistry and gives more precise physical meaning to the ideas of Langmuir on stoicheometry.

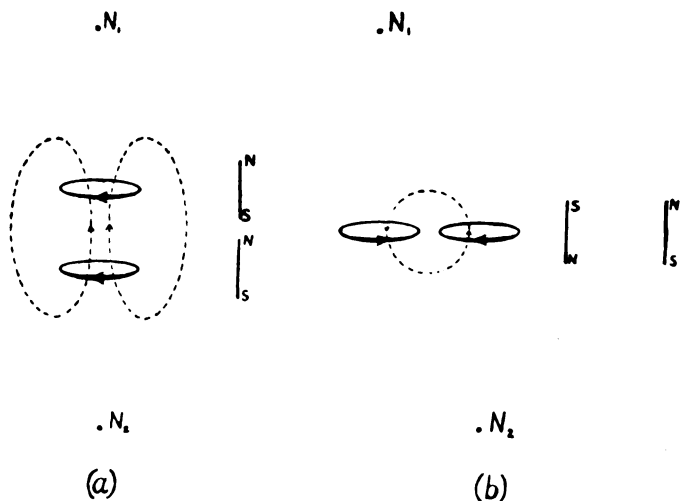
The valency bond is due to the attraction between two elementary magnets, electrons in small orbits, ring or vortical electrons. Either or both of the arrangements of fig. 1 may conceivably exist, their relative stability depending on the unknown dynamical conditions at such minute distances. The doublet in fig. 1 (*a*) is paramagnetic, in fig. 1 (*b*) diamagnetic. They exist where, in Langmuir's theory of chemical combination, electrons are "held in common." The combination of charged ions must be considered separately.

The condition that the electrostatic repulsion should vanish or be greatly exceeded by the magnetic attraction, demands

* Communicated by the Author. Substance read before the Manchester Literary and Philosophical Society, Nov. 29, 1921.

an oscillatory law of force at small distances. This postulate, apparently necessary to the continued existence of matter, has been advanced under several forms, *e.g.*, J. J. Thomson (Phil. Mag. vi. p. 220). The present hypothesis may be extended to atomic phenomena, from which a suitable law might be deduced. For the moment it is sufficient to postulate that, as two such magnetons approach, a point is reached where the electrostatic repulsion is counter-balanced by the magnetic attraction, at some distance small in comparison with infra-red wave-lengths, and depending upon the external field by which the positions of the electrons

Fig. 1.



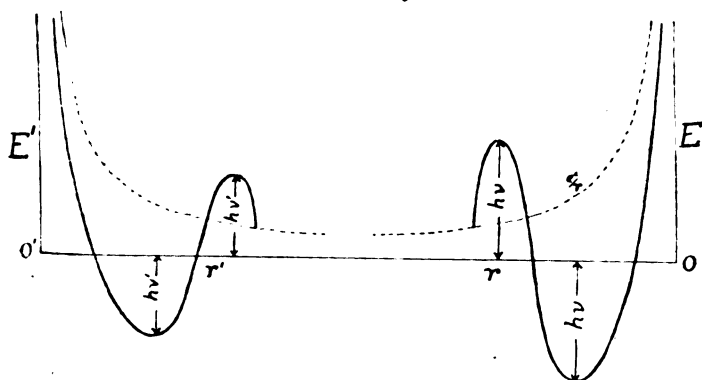
in the atoms are fixed. From this unstable state, the electrons will approach till the forces again attain equilibrium in a final stable position. The potential of the system at various distances is shown diagrammatically in fig. 2.

Returning to the doublets of fig. 1, the first point of importance is that electrostatic forces, however intense, of collision or of chemically active frequencies, will have no tendency to separate the constituent electrons. A doublet will scatter as a single particle with no effect on the bond. The only force affecting the two magnets differently is that due to a magnetic field normal to the axis of the magnets (perpendicular to the plane of the paper in fig. 1). When the natural period of oscillation is the same as that of an

incident radiation and sufficient amplitude attained, the similar poles will be brought into juxtaposition and the magnetic bond destroyed. The electrons will then move apart with an energy corresponding to their electrostatic potential at the point where magnetic equilibrium is reached. Radiation of the right frequency is the only means by which this bond can be destroyed.

The formation of a bond is the reverse process. The valency electrons, colliding with an energy equal to or greater than the critical potential energy of the bond, approach close enough for the magnetic attraction to predominate, and the compound is formed with absorption of the kinetic energy.

Fig. 2.



Consider, first, the simple case of uncatalysed dissociation or transformation, involving only one reactant molecule, in which the resultants are removed or do not react. This reaction is possible at any part of the molecular path, and its velocity depends simply on the energy density of the required radiation or that of the effective magnetic component. The observed effect of exterior illumination should be considerable, and, in fact, these reactions have provided the stock examples quoted by the adherents of the hypothesis. Several cogent arguments apply more particularly to such—*e. g.*, that reaction velocity is independent of dilution or expansion.

The simple act of combination is governed by entirely different factors. The electrons, constituting the bond, must be forced together, the electrostatic potential energy of the critical position being supplied at the expense of the kinetic

energy of thermal agitation. This must be in addition to the demands made by the elastic forces and radiation loss of an ordinary collision. The critical energy, w , may be identified as the critical increment which is used in deriving the Marcellin-Rice equation from the standpoint of thermal agitation. The expression AR/N is then equal to w and the velocity constant

$$k = se^{-\frac{A}{\theta}} = se^{-\frac{w}{h\theta}}.$$

The equation derived from the radiation hypothesis is $k = se^{-\frac{h\nu}{h\theta}}$, both being equivalent to the empirical law of Arrhenius $k = se^{-\frac{w}{h\theta}}$. Hence w , the potential energy of the newly-made bond, which is sensitive to the frequency ν , is equal to the quantum $h\nu$. The probability of the formation of the bond is determined by the thermal agitation and the velocity of a simple combination should not be affected by radiation.

These conclusions may be used as a criterion for the effect of illumination in any actual reaction. Combinations generally involve rupture of the original bond, and, in that regard, another factor must be considered. The temperature radiation principally occurs during collisions, so that, during the time when only reaction can occur, the sensitive molecule is subjected to radiation of a local intensity enormously above the statistical value at the temperature of the mass. This must very largely increase the effectiveness of the temperature radiation as compared with illumination for this type of reaction, quite independently of the particular physical picture we are considering.

The complete process of a reaction, in general, involves a double process for each valency electron. It must first be freed from its original state by absorption of a resonant radiation, then forced into the new state by absorption of thermal energy $h\nu$.

In an exothermic reaction, the lower frequency of the old bond would probably reach a saturation value in impacts sufficient to form the new bond of higher critical energy, and the reaction velocity be determined by the latter predominantly or entirely.

When the energy quantum of the original bond is the greater, the absorption of radiant energy of the necessary frequency will largely determine the rate of reaction. As far as the temperature radiation is concerned, this will occur principally during collisions. The effect of illumination

should be marked, though the relative effects of the two types are not necessarily proportional to their statistical density. This will depend on the rate of dissipation of the oscillatory energy of the magnetons. In all types of reaction, however, selective absorption or emission of active frequencies should be observable.

This criterion seems to accord with the observed facts as to the reactions whose velocity is increased by illumination. In general, photo-catalysis should be observable where the rate of reaction is determined by a dissociation. In the objection brought forward by Lindemann (*Phil. Mag.* Nov. 1920), concerning the hydrolysis of saccharose by hydrochloric acid, the reaction which determines the velocity is the formation of an unstable compound, a combination, which dissociates into the resulting sugars at a much greater rate, presumably as the active frequency is abundant in the temperature radiation.

In the dissociation of ozone into oxygen, the velocity and equilibrium depend on the dissociation of O_3 and the reverse dissociation of O_2 , also on the corresponding combinations governed by thermal agitation. This reaction, at constant temperature, is, and should be, affected by radiation of frequencies corresponding to both these bonds.

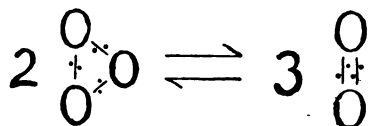
In the case of ionized compounds, it is presumed that electrons, superfluous to the stable system in the basic ion, have been transferred to complete that of the acid. This process may be regarded as the analogue of the combination in the former type of reaction. The compound is maintained by the general electrostatic attraction of the charged atoms, which corresponds to the force holding the valency electron to its nucleus in the unionized compounds.

The continued indication of quantum relations in such reactions suggests that the field of force, external to the atom, oscillates with the distance, giving definite positions of equilibrium. The frequency and energy of collisions should govern the combination and dissociation of such compounds, except in so far as they depend on the dissociation or combination of the constituent or resulting compounds of the former type.

Hence we see that this view of valency forces leads us to postulate, as a universal rule, quantum changes of energy in chemical reactions, with selective absorption and emission of the corresponding frequencies, but only in special cases, where the velocity is determined by the dissociation of an unionized compound, will any effect of exterior illumination

be observed. While giving due and equal importance to the two conflicting theories, it accords with the facts, qualitatively better than either, and quantitatively is generally identical.

In deriving this criterion for photo-catalysis, the critical state, which determines when the compound is made or destroyed, is the first unstable position of equilibrium in fig. 2. From this position, in the formation of a compound, it falls to the normal stable state with emission of radiation or, in dissociation, it is raised from that state by absorption of the characteristic frequency. If we assume that this corresponds to a change in potential of one quantum for each electron, the final energy change is the same as that postulated on the usual radiation hypothesis. The only difference is that the elementary energy change, $u = h(\nu - \nu')$, is associated, not with one molecule but with one valency bond. Thus, in the reaction of ozone $\rightleftharpoons$ oxygen, which we may write,



six bonds characteristic of ozone are replaced by six of oxygen, and the energy liberated $U = 6H(\nu - \nu')$ per mol or $u = 3h(\nu - \nu')$ per molecule of ozone decomposed, ν and ν' being the frequencies which are absorbed by and destroy the valency doublets of oxygen and ozone respectively. In general, the various changes of valency linkages may be deduced from the stoicheometric formula, and the expressions for the velocity constant and heat of reaction will become

$$k = se^{-\frac{h}{k\theta} \Sigma \nu} \quad \text{and} \quad U = H(\Sigma \nu - \Sigma \nu').$$

The frequencies ν and ν' are spoken of throughout as single frequencies characteristic of the bond. The actual facts cannot be so simple. Different original states of the constituent electrons with respect to their nuclei, such as are necessary to explain ordinary radiation phenomena, must result in a series of such frequencies. Sub-multiple quanta will be introduced if the equilibrium states of the electrons with respect to each other are quantized in a manner analogous to the atomic states. Each frequency in this complicated series of probabilities will be drawn out into a

narrow band owing to the variations in natural period imposed by the proximity of other molecules.

It does not seem that any reaction is sufficiently well known to identify with safety a particular frequency with its corresponding valency bond. Various attempts have been made, different writers making different choices, but strict quantitative application can hardly be expected till more is known about the simpler phenomena of the characteristic frequencies of the atoms themselves.

With regard to the form in which the energy of reaction is liberated, it must be noted that the greater part is as radiation of a frequency which is selectively absorbed. A portion of this will escape, the remainder be absorbed by the newly-formed bonds in a non-radiating condition and dissipated only by collisions with other molecules. The observations of W. T. David (*Phil. Mag.* Nov. 1921) that the maximum of infra-red emission is attained, in explosions, earlier than the maximum temperature are in marked accordance with this view.

Another phenomenon to be expected is the alteration of U and ν by solvents in non-stoicheometric catalysis. The above hypothesis demands intense inter-molecular magnetic fields (Oxley, *Phil. Trans. A.* 215, p. 79), so that the surrounding molecules of the solvent would change the natural frequency and potential of the magnetic doublet.

The valency bond is inextensible, a condition which seems to be demanded by the evidence of the specific heats of diatomic gases at high temperature. Dissociation cannot be caused directly by the most violent impact or tension, save by ionization—i.e., the attractive force between the magnetons is not affected, but one of them may be dislodged from its position in the atom.

This physical picture has proved valuable from so many points of view, and is supported by such a mass of evidence, chemical and magnetic, that it well deserves consideration in the not unreasonable expectation that it may be equally capable of explaining spectroscopic phenomena, which alone can define the necessary dynamical assumptions and put it to a crucial quantitative test.

XXXII. *On the Orientation of the Bohr-Sommerfeld Orbits.*

By ARTHUR W. CONWAY, F.R.S., *University College, Dublin* *.

IN the Bohr-Sommerfeld theory of elliptic orbits about a simple centre of force a difficulty at once appears to present itself. Selecting any line as z -axis and taking the usual polar co-ordinates (r, θ, ϕ) , the properties of the nucleus or of the space about it seem to cease to be isotropic. The structure of the various orbits is symmetrical about the z -axis. In fact, the normal to the plane of any possible orbit makes an angle with the z -axis whose cosine is $n_2/(n_2 + n_3)$ where n_2, n_3 are integers, being the partial azimuthal numbers. Or, put differently, the planes of all orbits which have the same azimuthal numbers envelope right circular cones. In what follows it will be shown that, by taking different coordinates, the orbits which have given azimuthal numbers touch a set of confocal quadric cones, the angle between the focal lines of which is at our disposal. The new coordinates, like the old (θ, ϕ) , are "separable." In fact, θ and ϕ are special cases. It is therefore necessary to add to Sommerfeld's criteria for the "selection" of orbits. It is necessary to specify the coordinates which have to be employed.

The cones

$$\frac{x^2}{a^2 - \lambda^2} + \frac{y^2}{b^2 - \lambda^2} + \frac{z^2}{c^2 - \lambda^2} = 0$$

represent confocal cones, the focal lines being given by

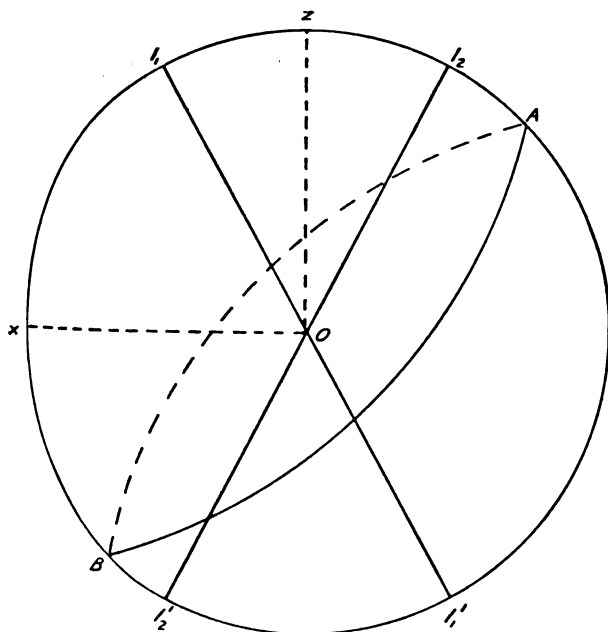
$$\frac{x^2}{a^2 - b^2} - \frac{z^2}{b^2 - c^2} = 0$$

($I_1 I_1'$ and $I_2 I_2'$ in the figure), where we take a, b , and c to be in descending order of magnitude. Through any point we have two values of λ^2 which we shall call λ^2 and μ^2 , such that $a^2 > \lambda^2 > b^2$; $b^2 > \mu^2 > c^2$. The μ -cones will surround OI_1, OI_2 and the λ -cones OI_2, OI_1' , with similar results for the other sheets of the cones. Let the plane of an orbit cut the circle of radius r through $I_1 I_2 I_1' I_2'$ in A and B. A certain μ -cone (μ_0) will touch this plane so that the whole range of μ for the orbit will be from $\mu = c$ to $\mu = \mu_1$, repeated four times. The range of λ will be from b to a repeated four times. Similar results will hold if A lies between I_1

* Communicated by the Author.

and I_2 . Taking as coordinates r, λ, μ we find for the square of the line-element

$$dr^2 + r^2(\lambda^2 - \mu^2) \left\{ \lambda^2 d\lambda^2 / (a^2 - \lambda^2)(b^2 - \lambda^2)(c^2 - \lambda^2) - \mu^2 d\mu^2 / (a^2 - \mu^2)(b^2 - \mu^2)(c^2 - \mu^2) \right\}.$$



If A is the Action Function we then get Jacobi's equation in the form

$$\frac{1}{m} \left(\frac{\partial A}{\partial r} \right)^2 + \frac{(a^2 - \lambda^2)(b^2 - \lambda^2)(c^2 - \lambda^2)}{m r^2 \lambda^2 (\lambda^2 - \mu^2)} \left(\frac{\partial A}{\partial \lambda} \right)^2 - \frac{(a^2 - \mu^2)(b^2 - \mu^2)(c^2 - \mu^2)}{m r^2 \mu^2 (\lambda^2 - \mu^2)} \left(\frac{\partial A}{\partial \mu} \right)^2 + \frac{2e^2}{r} - C = 0,$$

where m is the mass, $e, -e$ the charges on nucleus and electron, and $-C$ the energy constant. We then get the equations

$$\left(\frac{\partial A}{\partial \lambda} \right)^2 = mK \frac{\lambda^2(\lambda^2 - \mu_0^2)}{(a^2 - \lambda^2)(b^2 - \lambda^2)(c^2 - \lambda^2)},$$

$$\left(\frac{\partial A}{\partial \mu} \right)^2 = mK \frac{\mu^2(\mu^2 - \mu_0^2)}{(a^2 - \mu^2)(b^2 - \mu^2)(c^2 - \mu^2)},$$

where K is a constant. Hence, for the part of A which

depends on λ and μ we get

$$\begin{aligned} & \sqrt{mK} \int \lambda d\lambda \sqrt{\left\{ \frac{\lambda^2 - \mu_0^2}{(a^2 - \lambda^2)(\lambda^2 - b^2)(\lambda^2 - c^2)} \right\}} \\ & + \sqrt{mK} \int \mu d\mu \sqrt{\left\{ \frac{\mu_0^2 - \mu^2}{(a^2 - \mu^2)(b^2 - \mu^2)(c^2 - \mu^2)} \right\}}. \end{aligned}$$

Remembering the ranges of λ and μ we get the azimuthal equations

$$\begin{aligned} 2 \sqrt{mK} \int_{b^2}^{a^2} dz \sqrt{\left\{ \frac{z - \mu_0^2}{(a^2 - z)(z - b^2)(z - c^2)} \right\}} &= n_2 h, \\ 2 \sqrt{mK} \int_{c^2}^{\mu_0^2} dz \sqrt{\left\{ \frac{\mu_0^2 - z}{(a^2 - z)(b^2 - z)(z - c^2)} \right\}} &= n_3 h, \end{aligned}$$

where the variables λ^2, μ^2 have been changed to z . It will first be noticed that $n_2 h / \sqrt{mK}$ and $n_3 h / \sqrt{mK}$ are the periods of the elliptic integral

$$\int dz \sqrt{\left\{ \frac{(z - \mu_0^2)}{(a^2 - z)(b^2 - z)(c^2 - z)} \right\}}.$$

The sum of these periods is 2π , as may be seen by integrating with z , complex, about an infinite circle so that we get $(n_2 + n_3)h = 2\pi \sqrt{mK}$, from which the normal value of $-C$ can be deduced. Returning to the periods, they are certain transcendental functions of $\mu_0, f_1(\mu_0), f_2(\mu_0)$ (say), and so we have

$$f_1(\mu_0) = n_2 h / \sqrt{mK},$$

$$f_2(\mu_0) = n_3 h / \sqrt{mK},$$

$$\text{or} \quad f_1(\mu_0) / f_2(\mu_0) = n_2 / n_3,$$

so that if n_2 and n_3 are given, μ_0 is given and the orbit must touch the quadric cone

$$\frac{x^2}{a^2 - \mu_0^2} + \frac{y^2}{b^2 - \mu_0^2} + \frac{z^2}{c^2 - \mu_0^2} = 0.$$

XXXIII. *The Physical Interpretation of Relativity Mathematics.* By C. H. BICKERDIKE *.

EINSTEIN, in Chapter XII. of his little book on Relativity, p. 36, referring to the Lorentz transformations, says: "A priori it is quite clear that we must be able to learn something about the physical behaviour of measuring-rods and clocks from the equations of transformation, for the magnitudes x, y, z, s, t are nothing more nor less than the results of measurements obtainable by means of measuring-rods and clocks." It is quite evident that he means that rods in motion relatively to the observer could be ascertained by measurement to be shortened and clocks in motion could be ascertained to go slower than similar clocks at rest if the necessary delicacy of observation could be attained. If he does not mean that, it is difficult to know what the passage above quoted can be intended to mean.

In the whole book, however, there is no explanation of how such measuring and observing of the effects could conceivably be made, even on the supposition that the necessary degree of delicacy of observation or high degree of velocity could be obtained, although Einstein quite freely makes use of such suppositions for the purpose of explaining some aspects of his theory.

It is commonly supposed that practical difficulties are all that stand in the way of testing the contractions and slowings-down. It is here submitted, however, that that is not the case, and that, in fact, there is a confusion in speaking of the Lorentz transformations as giving information about the "physical behaviour" of clocks.

It is necessary to point out first of all the fundamental distinction between observation of certain predicted effects deduced from the elaborated general theory of relativity, such as the motion of the perihelion of Mercury and the bending of light, and observation of the alleged physical interpretation of the meaning of the Lorentz transformations. These transformations—and the equations of the general theory—may, and doubtless do, express important truths. The question still remains, however, whether it is truth about the behaviour of light and of other electromagnetic phenomena involving transference of forces across "space" or the "æther," or whether the truths relate, as Einstein says, to the physical behaviour of measuring-rods and clocks. It is the

* Communicated by the Author.

contention of the writer that at least as regards clocks and time the inference that the transformation of t and t' gives information as to their physical behaviour cannot be accepted.

So far as regards the main effect of the velocity of light in making the observations of one observer differ from those of another, it is easy to deduce from what is observed by S' what would be observed by S . There would be transformation equations connecting x and x' , t and t' , etc. No one suggests that these transformations are due to the physical behaviour of measuring-rods and clocks. It is found, however, that if we take the simple assumption of the constant velocity of light and the principle of moving axes, the transformation is not quite right. After allowing for the velocity of light as a constant, there is still a further small correction required, which is expressed by the Lorentz transformations. There is no *logical* necessity to assume that this transformation is consequent upon physical behaviour of clocks and rods. It may be that for some purpose of mathematical reasoning that assumption works sufficiently well. If it is to be taken literally, however, as a physical truth, the meaning in terms of what would be actually observed by numbers of observers in various circumstances, each recording what happened in his immediate environment, and subsequently comparing notes, requires to be explained before any clear meaning can be attributed to such phrases as physical behaviour of clocks and rods.

Eddington, in his 'Space, Time and Gravitation,' makes something like a realistic attempt to explain what the Lorentz transformations mean when translated into terms of what would be actually observed. It is submitted, however, that he stops short just at the point at which the explanation would begin to explain. His illustration of the aviator flying overhead at the convenient speed of 161,000 miles per second serves excellently to illustrate the point. The actual magnitude of the velocity is of no importance. The principle is exactly the same if we deal with smaller velocities. It saves time and trouble, however, to take the simplest illustration.

We are told, in the first place, that if he lay along the direction of his flight we on the ground should see him apparently only about three feet long, but the normal width—and he would have a strictly reciprocal impression of us if we lay on the ground in the direction of flight.

It is to be remarked that that is the only kind of *observation* of the effects of reciprocal motion which is ever definitely mentioned, and this relates only to contraction of length.

Eddington says, however, of the reciprocal shortenings : "It is not an illusion in the ordinary sense, because the impressions of both would be confirmed by every physical test or scientific calculation suggested." Presumably the "physical tests" must include measurements with clocks and rods. Yet we are never told how this could be done, and presently we shall see why.

It may be remarked in passing, however, as very interesting, that Eddington goes on to say : "No one knows which is right (*i.e.* the aviator or the observer on the ground), because we can never find out which, if either, is truly at rest in the ether." That seems to imply some clinging to the original idea of the FitzGerald-Lorentz contraction as a "real" contraction dependent upon absolute motion through the æther—*i.e.* motion relative simply to the æther and having nothing to do with motion relative to the observer. A contraction arising in that way might perfectly well be verifiable by measurement, but it would not be a strictly *reciprocal* effect of relative motion of two material bodies. In Einstein, there is no suggestion of clinging to this original conception of the FitzGerald-Lorentz contraction.

It is suggested that once the contraction is assumed to be a strictly reciprocal effect of relative motion, the whole idea of its being something physically measurable and verifiable is entirely destroyed. We have, however, first of all to consider further the question of the clocks.

Eddington's observer on the ground *calculates* that the aviator's clock goes slower than his own, and the aviator makes a similar calculation that the clock on the ground goes slow, and likewise each *infers* that the other's cigar is smoked more slowly than his own.

Eddington is careful to point out that the slowing of the clock is an inference and not an observation. "I say 'infer' deliberately ; we should *see* a still more extravagant slowing down of time ; but that is easily explained, because the aviator is rapidly increasing his distance from us and the light impressions take longer and longer to reach us. The more moderate retardation referred to remains after we have allowed for the time of transmission of light." The inference is therefore entirely dependent upon making the allowance for the velocity of light in the way which is assumed correct on the relativity principles, and this kind of observation therefore furnishes no possible means of verifying the correctness of the formulæ, or rather of the *interpretation* of the formula as giving information about the physical

behaviour of the clock and cigar when they are not immediately adjacent to the observer.

Eddington's discussion of the possibility of verification is confined to the question what would be observed if the aviator returned on his course, and he escapes the difficulty by pointing out that accelerations would have to be introduced and the discussion in question relates only to uniform motion.

For uniform motion—*i. e.* the restricted theory—the only possible verification can be by means of one or more additional observers stationary relative to the first.

If we introduce a second observer on the ground, the theory requires that, given what the first observer sees, in order to find what the second would observe, we have to imagine the origin of axes moved along to him from the first observer with the velocity of the thing under observation. That means, of course, that when the aviator passes over the second observer, the latter sees the aviator's clock showing just what the aviator himself sees.

In the absence of any discussion in books such as those of Eddington, Einstein's already mentioned, and Bolton's 'Introduction to the Theory of Relativity,' one might take it for granted that this means that the second observer would verify the calculation of the first observer, and, in fact, there can be no doubt that that is what is assumed to be the case, and that assumption is the foundation of what the public have regarded as the most striking mystery of the relativity theory.

It is submitted that the Lorentz transformation is open to a different interpretation. Before going into that, however, we will first consider some problems connected with circular motions. That means, of course, that we are no longer dealing with the restricted theory, and the reasoning about the reciprocal slowings of clocks is not quite the same.

The slowings connected with the restricted theory are not, however, something totally disconnected with the general theory. The restricted theory is a limiting case of the general theory, when gravitational fields are reduced to zero. If we start with no gravitational fields in existence and infer certain changes in lengths and times on the principle of the restricted theory, and then consider a case exactly parallel excepting that a small gravitational field is in existence, there is a difference between the changes of lengths and times to be inferred in the two cases, but a difference which must be proportionate to the strength of the field. We do

not, by introducing the gravitational field, suddenly abolish all the influence of mere relative motion.

Einstein, in his chapter on "The behaviour of clocks and measuring-rods on a rotating body of reference," indeed, begins his exposition by appealing to the results of the restricted theory. He supposes an observer on a Galileian reference system K (free from gravitational fields) to be observing a circular disk K' which is rotating, as judged by the observer on K . There is a clock at the centre of the rotating disk and one at the circumference. "As judged from this body (K), the clock at the centre of the disk has no velocity, whereas the clock at the edge of the disk is in motion relative to K in consequence of the rotation. According to a result obtained in Section XII., it follows that the latter clock goes at a rate permanently slower than that of the clock at the centre of the circular disk, *i.e.* as observed from K . It is obvious that the same effect would be noted by an observer whom we will imagine sitting alongside the clock at the centre of the disk."

From these facts Einstein *deduces* the inference that "in every gravitational field a clock will go more quickly or less quickly according to the position in which the clock is situated (at rest)."

In the case in question, the clock on the edge of the disk comes round again and again and can be observed from K over a period of time, and if the inference about slowing refers to "physical behaviour" of the clock, this slowing will be verified by the observer on K and would be also obvious to an observer alongside the clock on K' —who could see both his own clock and that of K at each moment of passing. It would then be properly described as a "real" slowing.

But we are equally entitled to say that, owing to the relative motion—which was the reason given for the slowing of the clock on K' —the observer on K' would infer that the clock on K went slow. The inference might not be that the *rate* of slowing inferred by K' with regard to K was exactly similar to that inferred by K with regard to K' . There is not the exact reciprocity of the restricted theory. K' , however, would infer a slowing and not an acceleration of the clock on K , by reason of the relative motion, and one or other or both would be found wrong.

It may be replied that the clock on the rotating disk being fixed to the disk is subject to stresses, and that no one knows what would be the effect of such stresses.

That is not a satisfactory answer, it is submitted. In the first place, we do not know that stresses of this kind must produce *any* effect at all, and if they did it is hardly likely that time-measuring instruments of all kinds would be affected alike. The centripetal force has direction and can hardly be supposed to affect uniformly in all directions the motions of parts of a mechanism. Any mere mechanical errors of that kind, moreover, should be discoverable and capable of correction.

The whole theory is based on the assumption that time can be measured by some kind of clock. How, otherwise, can any meaning at all be attributed to the symbols t and t' ? The theory as expounded is represented as meaning that *time* goes slower on the moving system, in the sense that all activities are slowed, not merely those of a clock of a particular make. The slowing of time is supposed to affect the rate of motion of all kinds of clocks, of cigar smoking, and of the activities of living organisms, and of the rate of vibration of atoms and electrons.

It is submitted that in the case cited this cannot possibly be a real observable effect, since K and K' cannot each find, on their periodically meeting, that these activities are all going slower for the other than they are for himself.

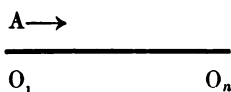
Let us take, however, the case of two equal disks rotating in opposite directions round the same axis with equal velocities, and let there be clocks fixed on the edge of each disk, with an observer at each. Now the centripetal forces or gravitational fields are of the same strength in each case and the magnitude of the stresses on the clocks is the same. How is it conceivable that, on the periodical juxtaposition of the two observers, each can see that the other's clock has gone slower than his own clock?

Another problem is this. Suppose K' rotates on an axis which is at rest relative to K , and there is a mark on the axis. K can measure time by the periodical passage of K' across this mark. K' can measure time by the periodical apparent alignment of himself between K and the mark. The instant at which K , K' and the mark would appear to be in a straight line would not be exactly the same for K and for K' , but the appearances of alignment would occur *with the same frequency* to both observers, and each can measure time by these recurrences. How, in that case, could it be said that "time" went slower for the one than the other? Why should not this phenomenon be the "clock" for each?

It is submitted that we are bound to look for some other meaning for the transformation of t and t' than "physical

behaviour" on the part of clocks, and incidentally that the inference from the general theory of relativity as to the slowing down of light-vibrations—the shift towards the red—need not be expected. If clocks do not slow down in any real sense, then vibrations of electrons not be supposed to so.

Reverting now to the restricted theory and Eddington's aviator. Let there be two observers on the ground, O_1 and O_n , the latter at a distance which would be covered by the aviator in 30 minutes, as measured by the clocks on the ground.



We have to ask what O_n , the second observer, would have to expect would be the time by the aviator's clock when the latter arrived at O_n . His origin of axes is, of course, on himself, and at the moment when O_n 's clock is at zero, he knows that the aviator is at a distance to the left, $-x$, moving towards him with a velocity V . He knows that O_1 's clock, at the same distance, but stationary, is at zero; but O_n does not agree that as between himself and the aviator it is zero time. He has to make his calculation as to what he "infers" to be the time by the aviator's clock. The velocities may be expressed in miles per minute, and the distance $-x$ is equal to $-30V$. According to the formula, t' the time "inferred" by O_n regarding the aviator's clock is

$$t - \frac{v}{c^2} x \qquad O + \frac{v^2}{c^2} 30$$

$$\frac{\qquad}{\sqrt{1 - \frac{v^2}{c^2}}}, \qquad \text{i. e.,} \qquad \frac{\qquad}{\sqrt{1 - \frac{v^2}{c^2}}},$$

which comes to $+15$. According to O_n , therefore, when his own clock is at zero, that of the aviator is already at $+15$, and as the aviator's clock is inferred to go at half the speed of O_n 's own clock, O_n should expect it to show $+30$ minutes when the aviator arrives and therefore to agree exactly with his own clock at that instant.

The assumption that the second observer would verify the calculation of the first is based, one may conjecture, on a confusion about changing the origin of axes. When they are changed from O_1 to O_n , *with reference to observation and inference about the moving system*, the zero of time is changed in one sense i. e. O_n attributes to the position of O_1 a different zero, but only so far as regards time on the

moving system. The mental change which I make in transferring the axes to O_n does not alter the physical fact that the clock of the stationary observer O_1 is still at zero. O_1 and O_n can and do have their clocks at zero at what they are agreed is, by definition, the same time, and the physical facts about their clocks are adjusted accordingly without reference to the existence of any aviator.

The inference of O_n about the aviator's clock can be nothing but a mathematical fiction. O_n is not there to see it at that moment. It is a mere matter of difference of definition between O_1 and O_n as to what they are to regard as zero time as between each of them and the aviator, and that difference of definition has no effect on the physical state of the clocks unless and until the parties agree to adjust the clocks according to the definition.

The physical facts as to the aviator's clock cannot be made to accord with *both* the definitions about zero time as between himself and O_1 and O_n respectively. The clock was actually set to agree, at zero, with O_1 . As regards O_n , the "inference" about the clock of the aviator going slow has no meaning excepting that what was correctly called zero as between the aviator and O_1 has to be called +15 as between the aviator and O_n .

It is submitted that what O_n would directly observe would be that the aviator's clock was at +30 when he reached O_n . He would not make any direct observation which would confirm the calculation of O_1 .

If there were likewise two aviators exactly the same reasoning must apply to them. They would not confirm one another's inferences.

The upshot is that so long as we regard only what is *directly* observed by a number of observers, as to what is visible and tangible in his immediate neighbourhood, and put together the results, we get the ordinary world of Euclidean space and absolute time. If we compare this with the analogy of blind men, "judging" by sound, but arriving at a conception of real motions by putting together the direct observations in which the finite and sometimes variable velocities of sound are eliminated, we should say that the result of the direct observations is entitled to be called the "real" or "physical" truth. Similarly it would seem, that whatever may be the truth expressed by the Lorentz transformations, it cannot be understood in any intelligible sense, that the transformation of t and t' gives us information about the "physical behaviour" of clocks.

Another point which may be considered is this. The

calculation of O_1 is that the aviator's cigar is smoked at only half the rate of O_1 's own cigar. But suppose the aviator holds his cigar in the line of his motion. It is "judged" by O_1 to be only half the length of O_1 's own cigar. At the same time it is inferred to be smoked only half-way through by the time O_1 has finished his cigar. On that supposition should not we say that the aviator is judged as smoking at only a quarter of the rate of O_1 ?

This consideration prompts another question about the clocks. There is no inherent reason why a clock should not have a pointer moving along a straight line instead of in a circle. Suppose the clocks are of this kind, and that, at rest, the pointer measures time by covering one inch per minute. The aviator has his clock with the straight-line dial in the line of his motion. To O_1 it "appears" that each inch on the aviator's clock is only half an inch, and in that sense his clock may be said to appear to go at only half the rate of the clocks on the ground. But the theory as expounded by Eddington and Einstein appears to imply that it would cover only half as many spaces as the clocks on the ground, and it might be said that it appeared to go at only a quarter of the rate of those clocks.

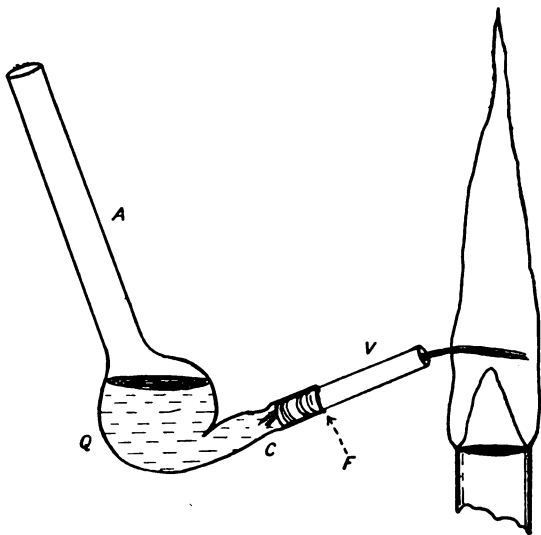
Should we not infer that the transformations embody some truth about the propagation of light between objects in motion relatively to one another and some truth about apparent contractions of length of objects in motion as seen by one observer only, who, therefore, can judge the length only by the apparent angle subtended, a contraction which, however, is not verified by comparison of observations by several observers, and which may be regarded therefore as analogous to an optical illusion—something additional to and different from what would be expected from the mere fact of the finite velocity of light?

The truth embodied respecting light implies also something about the state of the æther—or of space if we prefer that word—as affected by the motion of matter, and it is not surprising that this truth should have a bearing on all propagation of electromagnetic forces and also upon gravitation.

XXXIV. *On the Production of Coloured Flames for use with Spectrometers and Polarimeters.* By J. J. MANLEY, M.A., Research Fellow, Magdalen College, Oxford*.

THE apparatus represented in the accompanying figure has recently been designed and made for use with spectrometers and polarimeters. It is extremely convenient, requires but little attention, and by its means an intense flame coloration can be maintained for any desired period; the troublesome and unsatisfactory methods so frequently employed are thus entirely avoided. The apparatus is made in the following way:—

Near one end of a glass tube A about 1 cm. wide and 20 cm. long is first blown a bulb Q (fig. 1) having a capa-



city of 20 or 30 c.c.; then the short length of tube below the bulb is softened, drawn out, and bent at right angles to the larger limb A. In forming the narrower limb, care must be taken to make the diameter such that a portion of a "vitreosil" pipe V can be easily inserted. A suitable vitreosil pipe is one having a length of 8 cm., a diameter of 5 mm., and a bore of 1 mm. A constriction at C prevents the pipe from entering the tube for more than about 2.5 cm. The pipe with a few fibres of asbestos coiled upon it spiral-wise is introduced into the tube with a screw-like motion, the junction at F gently heated, and a little Faraday cement applied; a secure and liquid-tight union is thus effected. Finally, a bundle of 3 or 4 platinum wires, each 10 cm. long

* Communicated by the Author.

and 0.3 mm. in diameter, is placed within the pipe as shown. This bundle of wires constitutes a wick, the upper and free end of which is bent into a horizontal or even slightly downward position. Charging the bulb Q with the required solution and placing the exposed portion of the wick within a Bunsen flame as represented in the figure, an intense coloration is produced, and this as a result of the capillary action of the wires and pipe may be indefinitely maintained. If various flames are needed, it is convenient to construct several of the above-described feeders and to charge each with an appropriate solution : in this way the trouble caused by changing one solution for another and the cleansing of the apparatus, together with the consequent expenditure of time, may be avoided. The flame may be fed at very different rates by varying the inclination of the limb A. A suitable inclination, and therefore rate, is readily obtained by a corresponding rotation of the supporting clamp, which is not shown in the figure. To each solution should be added a very little hydrochloric acid. When the apparatus is not in use, A should be inclined so that a bubble of air appears at C.

Daubeny Laboratory,
Magdalen College,
Oxford.

XXXV. The Effect of Gases in facilitating the Passage of Current from an Electron-Emitting Source in Crossed Electric and Magnetic Fields. By Prof. O. W. RICHARDSON, F.R.S., and RABINDRANATH CHAUDHURI, M.Sc. (Calcutta), King's College, London*.

IT is well known that the passage of electron currents in vacuum tubes is stopped by the application of comparatively weak magnetic fields in directions perpendicular to the electric intensity. This is due to the curling up of the electron paths by the magnetic field, so that they intersect the emitting surface instead of extending to the anode. If, however, a trace of gas be admitted, so that the vacuum is no longer perfect, we find that the current will flow again, although its magnitude will in general be less than that obtained in the absence of a magnetic field. This effect occurs below the ionizing potential of the admitted gas, and therefore has nothing to do with the similar effect which occurs at higher potentials, owing to the formation of ions by impact ionization. The effect may be due to the combination of the electrons with neutral gas molecules to

* Communicated by the Authors.

form heavy negative ions (atomions), which pass to the anode, since their motion is little influenced by the magnetic field. However, it appears that almost anything which occurs at a collision will prevent an electron from returning to the emitting surface, in the type of apparatus used in our experiments at any rate; so that the passage of the current in a magnetic field is probably a test for any electron which has undergone a collision with a gas molecule, and not necessarily for one which has combined to form a negative ion. This should be borne in mind in reading the sequel, where the term "heavy ions" is sometimes used as an abbreviation for the "carriers of the current which succeed in reaching the anode in a transverse magnetic field great enough to stop the passage of electrons." These carriers behave from the experimental point of view like heavy ions would, and it is convenient to have a name for them; but we do not at this stage wish to commit ourselves definitely in all cases as to the detailed mechanism of the phenomena dealt with, and the name may turn out to be misleading.

We shall now consider the conditions which govern the passage of electrons between the electrodes in the absence of gas. The source of electrons was a tungsten filament of circular section (radius a) stretched along the axis of a cylindrical anode (radius b). The electric field (potential difference V) was applied between the hot wire and the anode, and the magnetic field H was parallel to the filament, so that the electric and magnetic fields were perpendicular to each other. Under these circumstances the electrons describe a curve similar to a cycloidal spiral about the filament, and the greater the magnetic field the less will be the maximum distance from the hot wire attained by an electron. The radial force due to the electric field at distance r from the axis can be written Ae/r when $A = V$ (volts) $\times 10^8 / \log \frac{b}{a}$.

Due to the current required to heat the filament (j amp.) there will be a magnetic field distributed in circles about the axis whose intensity is $\frac{B}{r} = \frac{2j}{10r}$. The equations of motion of the electron under these forces and that arising from the magnetic field H , parallel to the axis of z , will be

$$m \left[\frac{d^2 r}{dt^2} - r \left(\frac{d\theta}{dt} \right)^2 \right] = \frac{Ae}{r} + He \left(r \frac{d\theta}{dt} \right) - \frac{Be}{r} \frac{dz}{dt}, \quad (1)$$

$$m \left[\frac{1}{r} \frac{d}{dt} \left(r^2 \frac{d\theta}{dt} \right) \right] = -He \frac{dr}{dt}, \quad (2)$$

$$m \frac{d^2 z}{dt^2} = \frac{Be}{r} \frac{dr}{dt} \quad (3)$$

Integrating (3) subject to $\frac{dz}{dt} = w_0$ when $r=a$ and (2) subject to $\frac{d\theta}{dt} = \theta_0 = \frac{v_0}{a}$ at $r=a$, and substituting the values thus obtained for $\frac{dr}{dt}$ and $\frac{d\theta}{dt}$ in (1), gives

$$\frac{d^2r}{dt^2} = -\left(\frac{He}{2m}\right)^2 r + \left(av_0 - \frac{Heav_0}{2m}\right)^2 \frac{1}{r^3} + \frac{1}{r} \left[\frac{Ae}{m} - \frac{Bew_0}{m} - \frac{B^2 e^2 \log \frac{r}{a}}{m^2} \right], \quad (4)$$

$$= Lr + M \frac{1}{r^3} + N \frac{1}{r}, \text{ say.} \quad (5)$$

On multiplying by $\frac{dr}{dt}$ and integrating, subject to the condition $\frac{dr}{dt} = u_0$ when $r=a$,

$$\left(\frac{dr}{dt}\right)^2 = L(r^2 - a^2) - M\left(\frac{1}{r^2} - \frac{1}{a^2}\right) - 2N \log \frac{r}{a} + \left(\frac{Be}{m} \log \frac{r}{a}\right)^2 + u_0^2. \quad (6)$$

But, at the maximum distance of the electron from the axis, $\frac{dr}{dt} = 0$. If r be now taken as this maximum distance, then

$$L(r^2 - a^2) - M\left(\frac{1}{r^2} - \frac{1}{a^2}\right) + 2N \log \frac{r}{a} + \left(\frac{Be}{m} \log \frac{r}{a}\right)^2 + u_0^2 = 0. \quad (7)$$

Putting in the values of L, M, and N from (4) and (5),

$$\begin{aligned} & \frac{H^2}{4} \left(\frac{e}{m}\right)^2 r^2 \left(1 - \frac{a^2}{r^2}\right)^2 + \frac{Heav_0}{m} \left(1 - \frac{a^2}{r^2}\right) \\ &= 2 \log \frac{r}{a} \left[A \frac{e}{m} - \frac{Bew_0}{m} - \frac{B^2 e^2}{2m^2} \log \frac{r}{a} \right] \\ & \quad + v_0^2 \left(1 - \frac{a^2}{r^2}\right) + u_0^2, \quad (8) \end{aligned}$$

or, substituting the values of A and B in terms of V the

340 Prof. Richardson and Mr. Chaudhuri on the *Effect of* applied voltage and j the heating current in amperes,

$$\begin{aligned} & \frac{H^2}{4} \left(\frac{e}{m} \right)^2 r^2 \left(1 - \frac{a^2}{r^2} \right)^2 + \frac{Heav_0}{m} \left(1 - \frac{a^2}{r^2} \right) \\ &= \frac{2V \cdot 10^8 \cdot \frac{e}{m} \log \frac{r}{a}}{\log \frac{b}{a}} - \frac{2j}{5} \frac{e}{m} w_0 \log \frac{r}{a} \\ & - \frac{1}{25} j^2 \left(\frac{e}{m} \right)^2 \left(\log \frac{r}{a} \right)^2 + v_0^2 \left(1 - \frac{a^2}{r^2} \right) + u_0^2. (9) \end{aligned}$$

This equation, if solved for r , gives the maximum distance which electrons, or ions, having a given value of e/m can get from the wire for given values of H and V . If in addition we put $r=b$, we shall get the limiting relation between H and V which must hold in order that an ion starting from the filament may reach the surrounding electrode.

As it stands, equation (9), regarded as an equation for r , is not a very simple affair. It happens, however, that with the values of H and j employed in the experiments the various terms have very unequal values. The term linear in H and the term in j^2 are negligible, and the term in j is relatively small. To a first approximation we can also treat $\frac{a^2}{r^2}$ as small compared with unity. To this approximation, after putting in the numerical values for a , b , and e/m , equation (9) reduces to

$$H^2 = \frac{8 \cdot 39 V \log r / 005}{r^2} + 89 \frac{V_1}{r^2} \dots \dots (10)$$

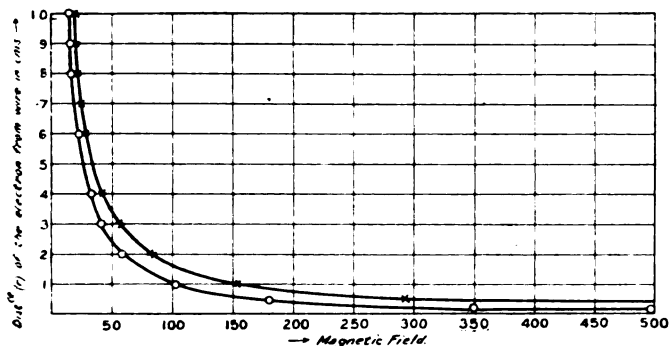
The values of H corresponding to different values of r given by this formula are shown in Table I. for V (the applied potential) = 4.2 volts and V_1 (the voltage equivalent of the emission velocity) equal to 0, 0.75, and 1.5 volts. The maximum emission velocity which is possessed by a measurable number of electrons is about 1 volt, and 1.5 volts can be safely taken as an upper limit for it. These values are only approximately correct, but they are accurate enough for the purpose of the present discussion. Any desired degree of accuracy can be obtained by keeping in more terms of equation (9) and proceeding in the same manner. Corresponding values of H and r for $V_1=0$, points $\bigcirc$, and $V_1=1.5$, points $\times$, are plotted in fig. 1.

TABLE I.

Applied Potential (accelerating) = $V = 4.2$ volts.

Value of r .	Magnetic fields required to bring the electron of different initial velocities to r .		
	H for $V_i = 0$.	H for $V_i = 0.75$.	H for $V_i = 1.5$ volt.
1.0 cm.	13.70	15.9	18.0
0.8	16.7	19.6	22.1
0.6	21.6	25.5	29.0
0.4	31.07	37.2	42.4
0.3	40.04	48.4	55.3
0.2	57.00	70.8	81.1
0.1	102.07	131.3	154.6
0.05	180.1	243.2	293.0
0.02	350.0	537.6	674.0
0.01	495.0	955.0	1260.0

Fig. 1.



From this figure we see that if a magnetic field of 160 units is used and the accelerating voltage between the filament and the cylinder is 4.2, the maximum velocity electrons will be confined within a distance of 0.096 cm. and the zero velocity ones within a distance of 0.06 cm. from the axis. This is on the supposition that the free movement of the electrons is not interfered with. If, however, the apparatus contains gas at a low pressure, encounters with gas molecules will occur, and as a result of such an encounter one of two things may happen. Either the electron will combine with the gas molecule to form a heavy ion which will travel to the anode in a slightly curved path under the combined fields—it would require a magnetic field of about 4000 units to stop an ion formed by the combination of a nitrogen molecule and an electron under these conditions,—or it will

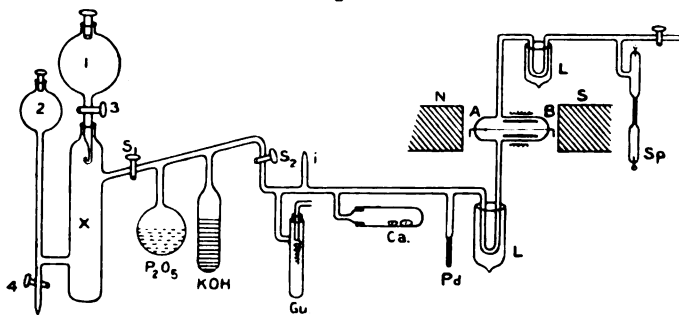
have its velocity suddenly altered so as to cause it to start to execute a new spiral path about an axis parallel to the magnetic field. The new path will not in general intersect the surface of the filament so that the electron will not return to the cathode, but neither will it intersect the surface of the anode. It will, however, in general be possible for such an electron to reach the anode as a result of a number of subsequent collisions. Thus we see that if gas is present, it will be possible for electrons to get through the magnetic field to the anode as a result of successive collisions with molecules as well as by combining with them.

Another advantage, as will be seen from fig. 1, of using fields as high as 160 units, is that the maximum distance of the electron and the corresponding length of the path is not very susceptible to small changes in the strength of the magnetic field in this region.

Experimental Arrangements.

The apparatus consists of a thermionic tube AB (fig. 2) placed axially between the poles of an electromagnet NS. The tube AB is connected on the one side with the gas-

Fig. 2.



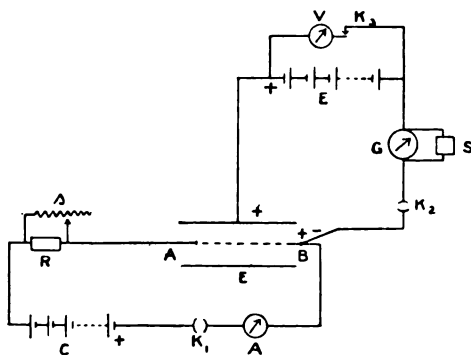
generating apparatus, and on the other with the spectrum tube Sp. and a phosphorus-pentoxide bulb, a mercury pump, and a McLeod gauge. On the two sides of AB are also two liquid-air traps LL.

The gas-generating part of the apparatus includes a palladium tube Pd for admitting hydrogen, a quartz tube containing two porcelain boats Ca containing calcium for absorbing gases, a glass tube Cu containing a spiral of copper wire which can be electrically heated for absorbing oxygen, and a set of apparatus X for generating nitrogen and other gases.

The thermionic tube AB consists of a cylindrical anode of thin copper 3.8 cm. long and 2 cm. in diameter, rigidly fixed in a glass tube. The cathode is a tungsten wire 3 cm. long and 0.01 cm. in diameter. By means of a suitable bow-spring, not shown in the figure, it is stretched taut along the axis of the cylinder, both when it is heated as well as when it is cold. In the preliminary preparation of the tubes the glass walls were heated as high as possible and the anode bombarded by an electron current from the hot wire whilst the gas was pumped away. Tests have also been made on similar tubes prepared by exhaustion in a vacuum furnace and then sealed off.

The electrical circuit is shown in fig. 3. The current for heating the filament AB is supplied by the battery C controlled by the resistance R, for which the shunt rheostat S

Fig. 3.



supplies a fine adjustment. The voltage driving the thermionic current is supplied by the battery E, the positive terminal of which is connected through the galvanometer G to the positive end of the hot wire. The potential difference between this point of the circuit and the anode is measured by the voltmeter V. The galvanometer G, used for measuring the thermionic current, had a sensitiveness of 1 division for 3×10^{-10} amp. For the larger currents the sensitiveness was reduced by means of the shunt S.

The magnetic field was produced by a large electromagnet. By varying the current through it the field between the poles, at 12 cm. distance, can be increased up to 1200 units. Before putting the tube AB in position, the field between the poles was explored. It was found that there was a residual field of about 10 units, and that when the current

was on, the field within 2 or 3 cm. on either side of the point midway between the poles was fairly constant.

The magnetic fields were measured by a coil and a fluxmeter. The coil used to measure the magnetic fields employed during the experiments consisted of 45 turns of silk-covered wire, wound on a cardboard cylinder which could be slipped over the thermionic tube AB. Before the tube was set up a certain magnetic field was established between the poles of the electromagnet and measured, using the standard coil supplied with the fluxmeter. The throw of the fluxmeter when the experimental coil was suddenly moved out of this same magnetic field was then measured. As a result of these measurements, it was found that 1 mm. deflexion of the scale, using the fluxmeter in combination with the experimental coil, was equivalent to 2 units of magnetic field, as nearly as the measurements could be made.

Preliminary Tests.

Before proceeding to the actual experimental tests, it is necessary to make sure that the tubes have been properly prepared. Tubes which have not been properly prepared are characterized by the possession of either or both of two defects. The first of these is the emission of positive ions and the second the emission of heavy negative ions, from the hot wire, under apparently good vacuum conditions. Both these conditions are readily recognized by carrying out preliminary experiments in the absence of gas, *i. e.* with as good a vacuum as the pumps used will maintain.

(1) *Positive ions.*—To test for these, reverse the potential of the battery E in fig. 3 so as to charge the cylindrical electrode negatively. Owing to the fact that the battery E is connected to the positive end of the hot wire and partly also to the emission velocities, if the applied potential difference V is small there will be a current through the galvanometer, which, however, will flow against the apparent applied electromotive force. This is due to the electrons, and will happen whether positive ions are present or not. If there are only electrons present, this current will fall sharply as the magnitude of V increases, and will, under our working conditions, disappear when V becomes equal to about -3 volts, and for greater negative voltages the current will remain zero. This is not the case if positive ions are present, for we then get a current carried by the positive

ions which flows in the direction of the applied electromotive force. Moreover, this latter current is unaffected by the application of a magnetic field, whereas the former is cut down to a small, or zero, value. The following numbers were given by a tube showing typical positive ion trouble:—

No magnetic field.

Applied Voltage.	0	-0.5	-1.0	-1.5	-2.0	-3.0	-4.0	-5.0	-6.0	-7.0
Current Reading.	24.1	22.8	13.8	3.9	0.8	-1.1	-1.7	-2.3	-2.5	-2.7

H=1000.

Applied Voltage.	0	-1	-2	-3	-4	-5	-6	-7	-8	-9
Current Reading.	0.0	0.0	-0.1	-0.6	-1.1	-1.5	-1.8	-2.0	-2.2	-2.3

If no positive ions had been present, all the negative values of current readings in the upper part of this table would have been zero, and all the current readings would have been zero in the lower table.

(2) *Negative ions.*—If these are present there will be a current to the anode, under high-vacuum conditions, in a strong magnetic field when the cylindrical electrode is positively charged, *i. e.* when the battery E is applied in the usual way. The following are typical data for a tube having this defect:—

H=1000.

Applied Voltage.	0	+1	+2	+3	+4	+5	+6	+7	+8	+10
Current Reading.	0.9	2.5	4.0	4.5	5.0	7.5	11.0	15.0	19.0	29.0

If no heavy negative ions had been present, the current readings would have all been zero under the conditions above.

In a properly prepared tube the phenomena just described are absent. Almost all the current from the hot wire to the electrode is carried by electrons. If a magnetic field is put on, the residual current will be very small if the pressure of the gas is small. This has previously been established by Owen and Halsall* with wires of iridium, palladium, and platinum, and by Richardson† with platinum. The following

* *Phil. Mag.* vol. xxv. p. 735 (1913).

† *Loc. cit.* vol. xxvi. p. 458 (1913).

346 Prof. Richardson and Mr. Chaudhuri on the *Effect of*
table gives typical results obtained by us with tungsten in
presence of traces of air and nitrogen:—

TABLE II.

Applied Potential 4.3 volts. Magnetic Field $H=160$.

Residual gas.	Pressure mm. of mercury.	Saturation Current without magnetic field. amp.	Residual Current with magnetic field. amp.	Current carried by electrons. amp.
Air	3×10^{-6}	$3600 \times 3 \times 10^{-10}$	$0.2 \times 3 \times 10^{-10}$	$3599.8 \times 3 \times 10^{-10}$
Air	6×10^{-6}	4800 ..	0.5 ..	4799.5 ..
N ₂	10^{-4}	700 ..	0.3 ..	699.7 ..

The following table gives data for a typical tube which has been satisfactorily prepared:—

TABLE III.

Gas pressure 10^{-4} mm.

Applied Potential.	Current without magnetic field.	Current with magnetic field $H=500$.
-6.0 volts	$0.0 \times 133 \times 10^{-10}$ amp.	0.0
-5.0 "	0.0 ..	0.0
-4.0 "	0.0 ..	0.0
-3.0 "	0.5 ..	0.0
-2.5 "	7.0 ..	0.0
-2.0 "	24.0 ..	0.0
-1.5 "	56.0 ..	0.0
-1.0 "	68.0 ..	0.0
-0.5 "	76.0 ..	0.0
0.0 "	77.0 ..	0.0
+1.0 "	77.5 ..	0.0
+2.0 "	77.7 ..	0.0
+3.0 "	77.9 ..	0.0
+4.0 "	79.0 ..	$0.2 \times 2 \times 10^{-8}$ amp.
+5.0 "	80.0 ..	0.3 ..

Initial amounts of heavy ions sensibly greater than in the proportion indicated by the figures at the bottom of the last column are inadmissible, and if they are present, further preparation of the tube should be proceeded with.

Experiments in Air.

The tungsten filament was 2.8 cm. long and 0.01 cm. diameter, the surrounding cylinder being 3.8 cm. long and

2 cm. diameter. The tube was first prepared so as to satisfy the tests described above on pumping out the gas to a pressure of 0.0001 mm. or less. On admitting air to a pressure of about 0.03 mm., currents were found to flow in the presence of a magnetic field. When these tests were made shortly after the tubes were prepared, the currents in a magnetic field were found to be somewhat irregular and to change with continued heating of the filament. The pressure of the gas was also found to change at the same time, probably owing to the absorption of oxygen by the hot tungsten. After letting in fresh air at a low pressure several times and heating the filament whilst pumping the air out, the filament seems to get seasoned to it, so that comparatively steady conditions may be obtained. We suggest that this may be due to the formation of a protective coating of oxide over the surface of the tungsten. The next table shows a set of typical figures obtained under these conditions.

TABLE IV.

Heating Current of the filament = 1.0 amp.
Applied Potential (accelerating) = 4.2 volts.

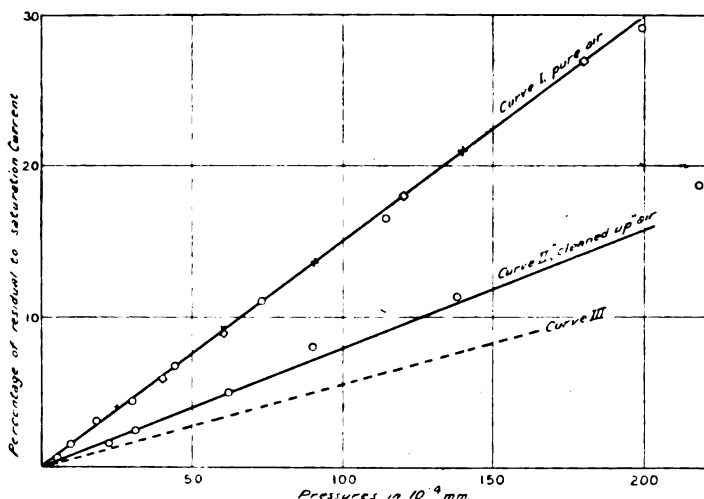
Pressure inside the tube.	Saturation Current without magnetic field.	Residual Current with magnetic field.	Magnetic Field.	Percentage of Residual to Saturation Current.
198×10^{-4} mm.	$2160 \times 3 \times 10^{-10}$ amp.	$630 \times 3 \times 10^{-10}$ amp.	164	29.2
114 "	2280 "	370 "	162	16.2
73 "	2280 "	250 "	162	11.0
44 "	2280 "	155 "	164	6.8
30 "	2280 "	100 "	162	4.8
18 "	2280 "	70 "	162	3.0
9 "	2340 "	35 "	162	1.5
5 "	2280 "	13 "	162	0.5

The maximum distance the electrons can get from the wire with the magnetic field used is a little under 0.1 cm., whereas the distance of the anode from the axis is 1 cm. The values at different pressures in the last column of this table are plotted against the pressure in Curve I., fig. 4, points O. It will be seen that the percentage is very closely proportional to the pressure of the gas. The other points near Curve I., viz. □ and ×, represent other series of observations taken under similar conditions.

If the wire is heated for a long time in the same air, the

percentage at a given pressure tends to diminish. This is probably due primarily to the absorption of the oxygen, but it may be due to some extent to the absorption of nitrogen also. A typical set of data after heating in air for a long time before taking the observations at successively lower

Fig. 4.



pressures is shown in fig. 4, Curve II. The dotted Curve III. of fig. 4 shows the lowest values of the percentage which we have been able to get in this way.

Experiments in Nitrogen.

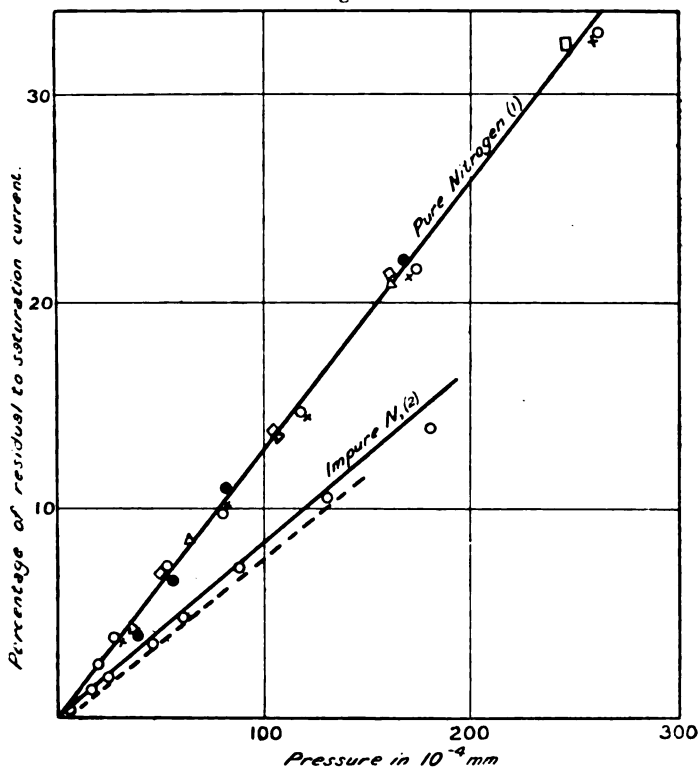
Two samples of this gas were tried, the first being commercial nitrogen supplied in cylinders by the British Oxygen Co., and the second nitrogen prepared chemically from ammonia.

When nitrogen was first admitted, similar phenomena were observed to those recorded with air. The pressure was found to diminish when the filament was heated and the anode bombarded with about 300 volts. After letting in fresh nitrogen a number of times and pumping it out with the filament hot, it was found that the pressure remained fairly constant under the experimental conditions.

A typical set of data got from the commercial nitrogen are shown in Curve II. of fig. 5. The heating current through the filament was 1.2 amp., the applied accelerating potential 4.3 volts, and the magnetic field ranged between

164 and 168 units. The percentage of residual to saturation current obtained with a given pressure of this sample of gas varied a little in the different experiments, doubtless owing to changes in the composition of the gas owing to the action of the hot filament on it. We have not analysed the gas,

Fig. 5.



but it probably contains argon and some traces of oxygen. The dotted line in fig. 5 shows the lowest set of values which we obtained with this nitrogen.

The chemical nitrogen was prepared in the apparatus shown in fig. 2. Pure ammonia solution was poured into vessel 2, which was filled up to the stopcocks 3 and S_1 . Pure bromine water previously boiled was placed in bulb 1 and poured into X by opening 3. The interaction produces nitrogen, which collects in the top portion of X. When X is about half full of nitrogen, S_1 is opened and the gas passes into the drying compartment. This dried gas is pumped

through the rest of the apparatus, and the process repeated several times before the sample of nitrogen which it is finally intended to test is stored in the compartment containing the phosphorus pentoxide and caustic potash. These agents remove any water vapour, ammonia, and bromine which may be mixed with the nitrogen. This convenient apparatus for preparing nitrogen free from air has been described by Waran*.

The stored nitrogen is let into the main testing apparatus in small quantities, the copper spiral being heated to take out any traces of oxygen which may have come from dissolved air in the liquids. Liquid air is kept on the traps to prevent access of bromine, ammonia, grease, mercury vapour or other vapours to the filament. The filament is heated, and the nitrogen let in and pumped out several times to get rid of any other occluded gases which may be present in the apparatus and to season the filament. The following data represent the result of a typical experiment made in this way :—

TABLE V.

Heating Current 1.35 amp.
Applied Potential (accelerating) 4.2 volts.

Pressure of Nitrogen.	Saturation Current without magnetic field.	Residual Current with magnetic field.	Magnetic Field.	Percentage of Residual to Saturation Current.
260×10^{-4} mm.	$522 \times 3 \times 10^{-3}$ amp.	$172 \times 3 \times 10^{-10}$ amp.	162	33.0
173 "	552 "	120 "	160	21.7
118 "	612 "	90 "	160	14.7
80 "	606 "	60 "	164	9.9
54 "	630 "	45 "	164	7.1
28 "	630 "	24 "	168	3.8
20 "	672 "	17 "	164	2.5

The values in the last column are shown plotted against those in the first, points O, close to the top line in fig. 5. Data given by four additional tests with nitrogen prepared in this way are also given. These data are all consistent with one another, and fall quite close to the line drawn. It will be observed that, for a given pressure, the percentage in pure nitrogen is greater than in the commercial nitrogen ;

* Phil. Mag. vol. xlii, p. 246 (1921).

it is furthermore intermediate between the values for pure air and for air which has been "cleaned up" by tungsten (fig. 4).

Conclusion.

The most interesting results of this investigation up to the present are the comparatively large magnitudes of the currents in the magnetic fields, the proportionality of these currents with the gas pressures, and the relative magnitudes of the effects in air and in nitrogen. These data would seem adequate to settle the nature of the phenomena in its main outlines. The fact that the residual currents are of similar magnitude in air and nitrogen suggests that the formation of heavy ions is a relatively unimportant factor. If it were important we should expect the effect to be much more marked in air, since oxygen is a much more electronegative gas than nitrogen. We are thus led to the conclusion that the passage of the currents in the magnetic field is a test of a collision between an electron and a gas molecule simply, and not of a collision which results in combination of the two to form a heavy ion.

The proportionality between the residual current and the gas pressure seems at first sight a difficulty on this view; on the ground that the co-operation of more than one collision is required for an electron to reach the anode. This suggests that the effect might be expected to increase more rapidly than as the first power of the pressure. It is probable, however, that this view of the phenomena is too superficial. The first collision will really decide the fate of the electron, because it puts it in a condition which prevents it from being returned to the cathode by the magnetic field. Since the experiments deal with a steady state, there is no opportunity for indefinite accumulation of electrons or ions in the field; so that the only alternative is for the electron to reach the anode. If the gas present is inadequate to ensure this by means of collisions, it seems likely that the electrons present in the space will cause a readjustment of the electric field in such a way as to make this possible. On this view, the currents to the anode in a magnetic field will be proportional to the probability of a single collision, and therefore proportional to the gas pressure, for small pressures.

The actual magnitudes of the currents in a magnetic field are also consistent with this point of view. On the assumption that the occurrence of a single collision is sufficient to determine the passage of an electron to the anode, we can

352 *Effect of Gases on the Passage of Electric Currents.*

estimate a value for the mean free path of an electron in the gas. To do this, we require to know the length p of the path of an electron in the magnetic field when no collision occurs. As an approximate illustration let us take this to be an arc of a circle whose diameter is along the axis of the cylinders, and whose radius is equal to the maximum distance r which the electron travels from that axis. Then

$$p = r(\pi - 2 \sin^{-1} a/r),$$

a being the radius of the hot wire. The proportion of any group of electrons which travel a distance x without collision and then collide in the succeeding distance dx is

$$e^{-\frac{x}{\lambda}} \frac{dx}{\lambda},$$

and the proportion ξ which collide in a path of length p is thus

$$\int_0^p e^{-\frac{x}{\lambda}} \frac{dx}{\lambda} = 1 - e^{-\frac{p}{\lambda}}.$$

Thus

$$\lambda = -p / \log_e(1 - \xi).$$

For $H=160$, r lies between the limits 0.06 and 0.096 cm. according to the value of the initial velocity of the electron. If we take $r=0.08$ cm. as a mean value, this gives $p=0.08 \times 3.015$ cm. At a pressure of 0.02 mm. of mercury the value of ξ was 0.259.

On substituting these numbers, we find

$$\lambda = 0.805 \text{ cm. at } 0.02 \text{ mm. pressure,}$$

or

$$\lambda_0 = 2.1 \times 10^{-5} \text{ cm. at } 760 \text{ mm. pressure.}$$

The last number is similar to those given by other methods. On account of the approximate nature of some of the assumptions made, no correction has been applied for the influence of the high temperature of the gas on its density under a given pressure.

If the preceding interpretation of the phenomena is substantiated by further experiments, it would seem that the method might be used to compare and perhaps to measure the mean free paths of electrons in different gases. Further experiments extending to a number of gases are in progress by one of us (R. C.), and will be reported upon shortly.

XXXVI. *The Ionization by Collision of Hydrogen, Nitrogen, and Argon.* By T. L. R. AYRES, B.A., M.Sc., Exeter College, Oxford*.

1. **T**HE principal object of these experiments was to determine the ionization in hydrogen, nitrogen, and argon, by collisions of electrons with molecules for comparatively small values of the ratio of the electric force X to the gas-pressure p . The range specially examined is from $\frac{X}{p} = 5$ to $\frac{X}{p} = 60$, X being in volts per centimetre and p in millimetres of mercury.

In the original determinations of the number of ions generated by collision in these gases†, the effects of positive and negative ions were not measured in cases where the values of $\frac{X}{p}$ were less than about 40.

The velocities in the direction of the electric force, and the mean velocity of agitation of the electrons in these gases, have been found recently by Professor Townsend and Mr. V. A. Bailey‡ by a method which had previously been used to determine the motion of electrons in air.

Their range of investigation extended from $\frac{X}{p} = 0.25$ to $\frac{X}{p} = 60$ or 100; consequently, the determination of the number of ions generated by collision within this range is an allied question of considerable interest.

The number of ions generated by collisions of electrons with molecules, and the total number of collisions of electrons with molecules, would then be known for cases in which the mean velocity of agitation and the mean velocity in the direction of the electric force can be measured accurately.

When the original researches on ionization by collision were published, the term "ion" was generally applied to any small particle with an atomic charge, and included

* Communicated by Prof. J. S. Townsend, F.R.S.

† J. S. Townsend, *Phil. Mag.* iii. p. 557 (June 1902), and (6) vi. p. 598 (Nov. 1903). H. E. Hurst, *Phil. Mag.* (6) xi. p. 535 (1906). E. W. B. Gill and F. B. Pidduck, *Phil. Mag.* xvi. pp. 280-290 (Aug. 1908).

‡ J. S. Townsend and V. A. Bailey, *Phil. Mag.* xlii. p. 874 (Dec. 1921), xliii. p. 593 (Mar. 1922), and xliv. p. 1033 (Nov. 1922).

electrons as well as particles with masses of the order of the mass of a molecule.

At present, the term "ion" is generally applied only to the larger particles in order to distinguish them from electrons.

For brevity, it is frequently desirable to retain the original notation; so that when a pair of ions are said to be generated by a collision, what is meant exactly is that a positive ion and an electron are generated when a positive ion or an electron collides with a molecule. The original experiments afford ample evidence that with these forces and gas-pressures the electrons move freely, and are not combined with molecules of the gas. Also the ratio of the charge to the mass of the negatively charged particle shows that in the process of ionization by collision the negative particles which move along the free paths between collisions with molecules are electrons, as they have a mass of from one- to two-thousandth of the mass of an atom of hydrogen*.

2. In these experiments ultra-violet light was used as the ionizing agent and, as in the earlier experiments†, it was found that the current produced could be represented by the equation

$$n = n_0 \frac{(\alpha - \beta) \epsilon^{(\alpha - \beta)a}}{\alpha - \beta \epsilon^{(\alpha - \beta)}} \dots \dots \dots (1)$$

when both positive and negative ions were actively engaged in the production of new ions by collision. Whilst, in weaker fields, before the positive ions have acquired sufficient velocity to be effective in this direction, the equation for the current becomes

$$n = n_0 \epsilon^{aa} \dots \dots \dots (2)$$

Equation (2) proves sufficient for work up to $\frac{X}{p} = 15$ for argon, 30 for hydrogen, and the neighbourhood of 100 for nitrogen.

The usual nomenclature of the collision-theory is adopted without further explanation; and all symbols usually employed are retained in their usual form and with their usual meaning.

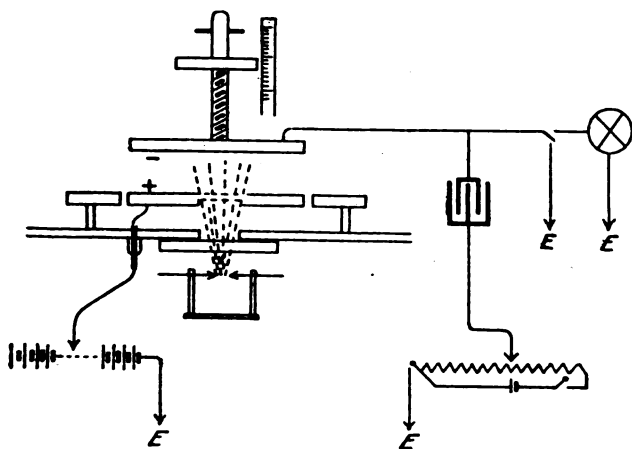
* J. S. Townsend and H. T. Tizard, Proc. Roy. Soc. A. lxxxviii. p. 336 (1913).

† Townsend, 'Electricity in Gases,' Chaps. VIII. to X.

3. The apparatus consisted essentially of a pair of well-insulated parallel-plate electrodes of silver, with guard-ring, in an exhaustible glass bell-jar. The centre part of the lower plate was pierced with parallel slits, in order to form a grid allowing of the admission of ultra-violet light from below to the ionization-chamber. The distance between the plates was accurately adjustable by a micrometer-screw worked from outside through a well-fitting socket. The slits in the lower plate were about $\frac{1}{4}$ of a millimetre wide, 1.5 cm. long, and 1 mm. apart. The diameter of the upper movable plate was 6 cm., and the maximum distance between the plates 1 cm.

The general arrangement of the apparatus is shown by the diagram in fig. 1, which will sufficiently explain itself.

Fig. 1



In the earlier experiments the electrodes were usually made of zinc, but it was considered desirable to use silver in these experiments to see if the determinations were affected by changing the metal of the electrodes. The recent experiments of Townsend and Bailey on the motion of electrons in argon showed that that gas is extremely sensitive to small quantities of impurities, and they found it advantageous to construct their apparatus, using glass instead of ebonite as an insulator.

The same precautions were taken in the apparatus used in these experiments, all electric insulation being effected by means of glass supports.

The contact of sealing-wax and grease with the gas

was reduced to a minimum by having ground-glass joints with the wax outside, wherever a fused glass joint was impossible. The electric leads were admitted through capillary tubes which fitted into carefully ground sockets, and the wires were sealed into these only in the outer half of the tube.

The object of these precautions—prevention of contamination of the gas—appears to have been fairly successfully attained, if one judges by the steadiness of the gas-pressure and the uniformity of the observations in the case of the hydrogen and nitrogen.

The currents were measured by the Induction Balance method* generally used in these experiments, and all wires, the electrometer, condensers, and glass jar were well screened.

4. The gases were prepared by the following methods:—

Hydrogen. A palladium tube was fused into the glass tubing of the apparatus and surrounded by an exhaustible silica sleeve. This sleeve was attached to a voltmeter for the production of the gas by the electrolysis of barium hydrate, and pure hydrogen was admitted to the apparatus through the palladium by applying heat outside the sleeve.

Nitrogen. This gas was produced chemically by very slightly warming a mixture of equal parts of sodium nitrite, ammonium chloride, and potassium bichromate in three parts of water. The gas was then passed successively over KHO , H_2SO_4 , and heated metallic copper.

In each case the gas was stored in a flask over P_2O_5 and allowed to stand for at least a week.

Argon. The gas used in these experiments was a specimen of that which had been carefully purified for the experiments on the velocities of electrons referred to above, and the results of those experiments show that impurities probably amounted to less than .01 per cent. A flask containing the specimen of pure argon was sealed to the apparatus, and the gas admitted by means of a mercury-sealed tap.

5. After repeatedly exhausting and washing out the apparatus with pure gas, the ionization experiments were carried out with gas-pressures ranging up to about 100 mm., and electrode-distance up to its full amount whenever possible.

* J. S. Townsend, Phil. Mag. (6) vi. p. 598 (Nov. 1903).

6. These experiments were made over large ranges of electric forces and gas-pressures, in order to compare the results with those of the earlier investigations. It will be seen that the present results are in good agreement with the earlier ones in hydrogen and nitrogen; but in the case of argon the agreement was not good in the determinations corresponding to the lower values of the ratio $\frac{X}{p}$.

7. The ratios $\frac{\alpha}{p}$ and $\frac{\beta}{p}$ corresponding to different values of $\frac{X}{p}$ are shown in Tables I., II., and III. The distance S , at which sparking should occur, calculated from the equation

$$\alpha - \beta e^{(\alpha - \beta)S} = 0,$$

affords a means of comparing the sparking-potential V , obtained experimentally, with the calculated sparking-potential XS .

Tables I. to III., and the curves in figs. 2, 3, 4, 6, and 7, give a general survey of the results obtained; whilst the results obtained with the lower values of $\frac{X}{p}$ are represented on a larger scale in the remaining figures.

8. In order to detect any leakage of air into the apparatus tests were regularly made, each of several days' duration, after each series of observations. The apparatus was completely exhausted and the McLeod gauge watched. The leakage was always so small as to be negligible, when it is remembered that the gas was rarely more than a few hours in use. After that it was always pumped out into the air, and fresh gas taken for the next series of observations.

9. Special reference, however, must be made to the effect of impurities upon the behaviour of argon.

When this gas was examined by Gill and Pidduck, their specimen was probably not of the highest purity. There was a leakage in the apparatus of .01 mm. per day, but they found it did not appreciably alter the electrical properties of the gas.

It will be seen from the results of the present investigation

that a very small quantity of impurities affects the electrical properties of pure argon, but that there is no similar effect in pure hydrogen or nitrogen.

Gill and Pidduck also made experiments with helium* which showed that its electrical properties were much affected by impurities, and, in consequence, a second investigation was made with much more carefully purified gas. The difference in the results was remarkable, and bears a very strong resemblance both in nature and magnitude to the difference between very pure and slightly impure argon observed in the present investigation.

During the period of the experiments with argon, the leakage tests referred to in the preceding section never showed a greater rate of leakage than $\frac{1}{10}$ mm. in five weeks (*i. e.* less than $\frac{1}{1500}$ mm. per day). The contamination due to this during the period of two hours, over which determinations generally extended, must therefore have been quite negligible.

In these first few hours, however, measurable changes in the electrical properties of argon were found to take place on each occasion.

It seems probable that the cause of these changes was the vaseline-lubricant used in the air-tight socket through which the micrometer of the present apparatus was worked. This explanation is strengthened by the fact that Townsend and Bailey, although using a distinctly more sensitive apparatus in their recent work with argon, found a considerably less tendency in pure argon to change in the first few hours. Their apparatus was free from the above-mentioned possible source of contamination.

10. Under these circumstances, speed of measurement was essential; and it was found possible, by working at three definite distances (3, 6, and 9 mm.) between the electrodes, to take quite a large number of readings within an hour of the entry of the gas to the ionization-chamber.

If the gas was retained in the chamber for a few days the values of α and β became stationary, and after five weeks no further changes were observed.

11. The experiments for the pure and the slightly impure gas were made over the whole range of forces and pressures

* E. W. B. Gill and F. B. Pidduck, *Phil. Mag.* xvi. pp. 280-290 (Aug. 1908), and xxiii. pp. 837-848 (May 1912).

corresponding to $\left(\frac{X}{p} = \right) 0.8$ to 600; and it was found that above 200 the $\frac{\alpha}{p}$ values differed very little from those of the earlier investigators.

The $\frac{\beta}{p}$ factor for the positive ions was, however, always much higher than theirs—a fact which is confirmed by the low sparking-potentials which were obtained in these experiments.

Of necessity, during any series of readings, close approach to the sparking-potential had to be rigidly avoided. Economical usage of the gas also required that the observations of sparking-potentials should, in general, only be taken after using the gas for an hour or so. A few sparking-potentials were, however, taken with pure gas fresh from the storage flask.

12. The mean results of the determinations for hydrogen and nitrogen are given in the following tables:—

TABLE I.
Hydrogen.

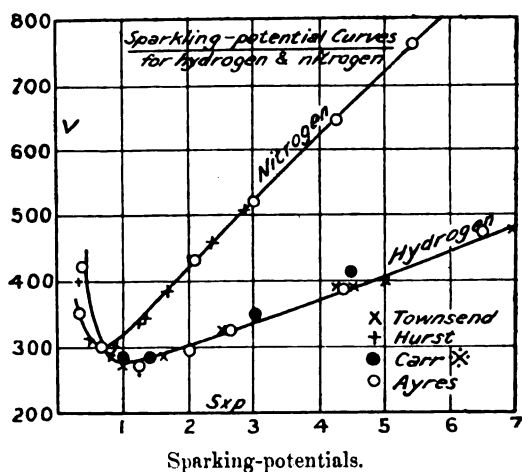
$\frac{X}{p}$	$\frac{\alpha}{p}$	$\frac{\beta}{p}$	$S \times p$	XS.	V.
5	0060				
10	0105				
15	0177				
20	0243				
25	0367				
30	0726	00015			
40	194	00065			
50	354	0016			
60	560	0030	9.40	564	570
80	970	0068	5.15	412	412
100	1370	0116	3.50	350	351
125	1800	0215	2.50	313	315
150	2.12	0365	1.96	294	294
175	2.41	0560	1.61	282	283
200	2.63	079	1.38	277	277
300	3.30	200	.91	273	272
400	3.65	325	.73	292	291
500	3.92	455	.63	315	313
750	4.32	74	.49	367	363
1000	4.60	92	.44	438	420
2000	4.88	130			
3060	4.95	147			

TABLE II.
Nitrogen.

$\frac{X}{p}$	$\frac{\alpha}{p}$	$\frac{\beta}{p}$	$S \times p$	XS.	V.
5					
10	011				
15	0170				
20	0239				
25	0305				
30	0382				
40	0550				
50	0820				
60	121				
80	257	0000			
100	471	0002			
125	850	0013	7.65	956	965
150	1.32	0048	4.27	641	648
175	1.84	0084	2.95	516	518
200	2.50	013	2.12	424	425
300	4.10	058	1.06	318	318
400	5.43	103	.75	300	298
500	6.29	157	.60	300	302
750	7.91	301	.43	323	322
1000	9.02	422	.36	357	350
2000	11.24	683			
3000	12.10	804			

13. The results of the experiments are shown by the curves in figs. 2, 3, and 4. The points marked in the diagrams give the results of the earlier investigators.

Fig. 2.



* W. R. Carr, Phil. Trans. A. cci. p. 403 (1903).

Fig. 3.

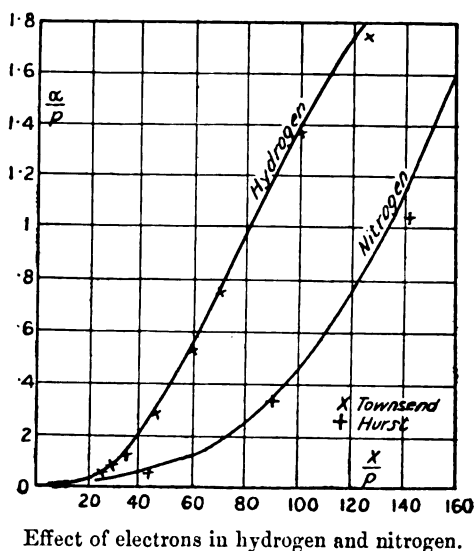


Fig. 4.

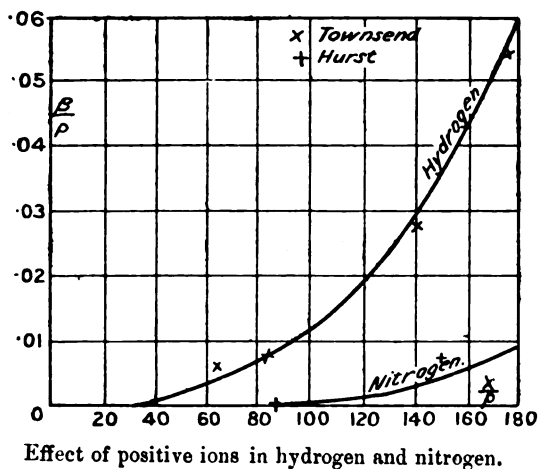
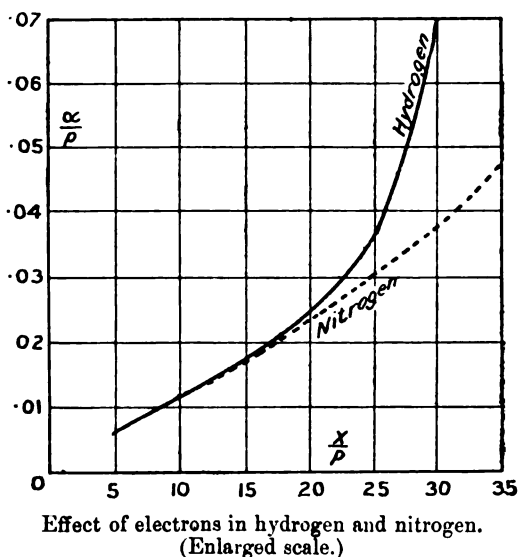


Fig. 5.



It is desirable to emphasize the fact, that, although the observations represented in the foregoing figures are expressed as the ratios $\frac{X}{p}$, $\frac{\alpha}{p}$, $\frac{\beta}{p}$, yet each particular value found was

the result of a number of different observations (generally about 10) at pressures as diverse as possible. The ratios so obtained were approximately equal, and it is their mean values which are finally given in this paper.

14. Table III. shows the results obtained for Argon on the same plan as the previous tables.

TABLE III.
Argon (pure).

X p	$\frac{a}{p}$	β p	$S \times p$	$XS_{(calc.)}$	V
2	005				
5	075				
10	182	0000			
15	300	00067			
20	440	00164	12.8	256	
25	550	00278	9.87	247	
30	700	0039	7.52	226	218
40	960	0064	5.25	210	208
50	1.22	0089	4.08	204	203
60	1.48	0114	3.32	199	200
70	1.738	0140	2.80	196	197
80	1.976	0167	2.44	195	195
90	2.220	0195	2.16	194	194
100	2.45	0223	1.94	194	194
125	3.02	0290	1.552	194	193
150	3.567	0371	1.295	194	193.5
175	4.11	0450	1.111	194	194
200	4.64	0546	.970	194	194
300	6.40	.100	.661	198	198
400	7.80	.160	.511	204	(205)
500	8.70	.235	.428	212	(211)
600	9.35	.330	.374	220	(225)

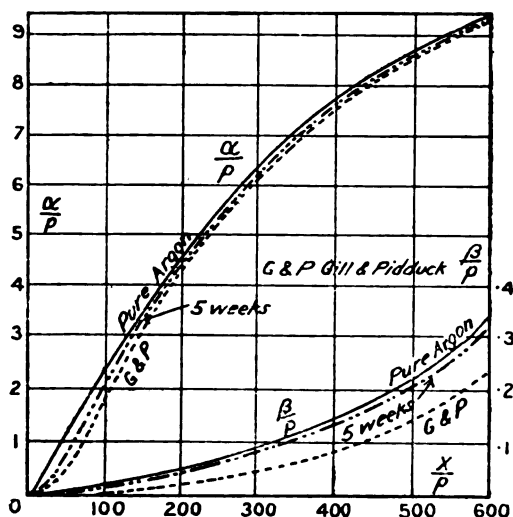
TABLE IV.
(Argon).

	p	S	$S \times p$	V
(a)	.97	1.0	.97	194
	2.10	1.0	2.1	194
	5.2	1.0	5.2	210
(b)	.41	1.0	.4	207
	2.08	.5	1.04	200
	2.08	.8	1.66	198
	2.08	1.0	2.08	202
	5.21	.6	3.12	210
	5.21	1.0	5.21	224
	9.00	.7	6.3	226
	9.00	.9	8.1	234
	9.00	1.0	9.0	232
	15.0	.8	12.0	242

The actual sparking-potentials found experimentally in Argon are shown in Table IV. (a) with pure gas just admitted to the ionization-chamber; (b) with gas which had been in use for about an hour in ionization experiments.

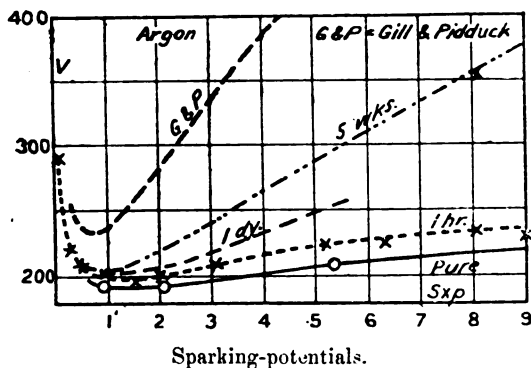
15. The numerical results given in the preceding tables for Argon are represented graphically in the following figures:—

Fig. 6.



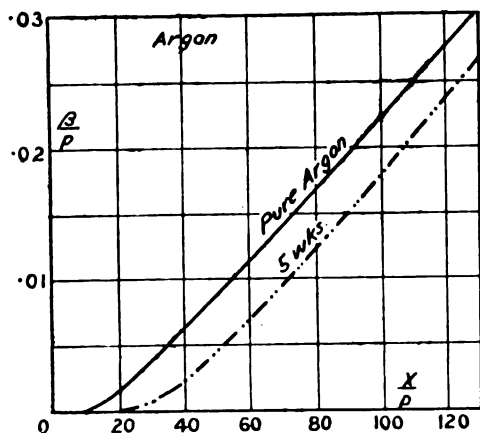
The continuous curve represents results obtained with pure Argon. The lower dotted curve gives the results obtained by Gill and Pidduck, whilst the intermediate curve shows values of the ratios after the gas had stood in the ionization-chamber for 5 weeks.

Fig. 7.



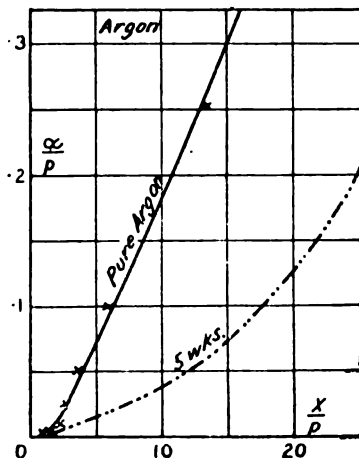
The change in the sparking-potential due to impurities was more rapidly evident than in other measurements. Fig. 7 shows by a continuous curve determinations obtained with the pure gas. The intermediate dotted curves indicate the effect of very slight impurities at certain approximate intervals of time up to 5 weeks.

Fig. 8.



Effect of positive ions in pure Argon and in Argon which was slightly impure.

Fig. 9.



Effect of electrons in Argon. (Enlarged scale.)

16. For certain gas-problems information given in the ratio form of Tables I., II., and III. is insufficient. Consequently, for the purpose of supplying exact data as regards the actual pressure, distance between electrodes, maximum voltage, &c., a number of actual examples from each gas are tabulated in the order of the ratio $\frac{X}{p}$ in Table V.

TABLE V.
Argon.

$\frac{X}{p}$	X.	p.	a.	v.	α .	β .	t.
1.05	63	60	.9	56.7	.063	—	10
2.14	34.2	16	.9	30.8	.132	—	15
2.56	41	16	.9	36.9	.389	—	20
3.50	55.9	16	.9	50.3	.817	—	5
5.95	95.1	16	.9	85.6	1.523	—	10
13.4	69.4	5.21	.9	62.5	1.303	—	5
33.3	173.3	5.21	.9	156	3.527	.0268	60
40.0	208	5.21	.9	187	5.05	.0355	0
40.0	208	5.21	.9	187	4.63	.0303	60
* 74.6	190	2.55	.8	152	4.74	.0389	10
97.5	248.5	2.55	.8	196.5	5.142	.0415	10 dys
192	252.4	1.325	.7	176.7	5.762	.0620	60
349	292	.838	.6	174.5	5.87	.108	33 dys
507	323	.638	.6	194	5.67	.167	15
* 613	229	.374	.8	183.2	3.52	.119	33 dys
* 621	396	.638	.5	198	6.02	.220	30

Hydrogen.

5.15	51	9.9	1.0	51	.063	—
10.3	102.5	9.9	1.0	102.5	.105	—
26.0	204	7.85	1.0	204	.311	—
50.3	206	4.1	1.0	206	1.515	.0053
* 73.6	301.5	4.1	1.0	301.5	2.42	.023
124.2	122	.985	1.0	122	1.720	.0203

Nitrogen.

9.7	112	11.5	1.0	112	.128	—
24.8	61.5	2.48	1.0	61.5	.075	—
61	915	15	.5	458	1.91	—
* 165.2	410	2.48	.9	369	4.13	.0176

A few examples are then given illustrating the degree of closeness of the theoretically calculated currents [using equations (1) or (2)] to the currents measured experimentally.

The symbols employed have the following meaning :

X = field-strength in volts per cm.

p = gas-pressure in mm.

a = distance apart of electrodes in cm.

v = maximum voltage difference employed.

e = ϵ° .

$$E = \frac{(\alpha - \beta) e^{(\alpha - \beta)a}}{\alpha - \beta e^{(\alpha - \beta)a}}.$$

α, β = the number of pairs of ions produced per cm., by collision, by one negative or one positive ion respectively.

t = time in minutes after first admission of gas to chamber.

q = the current observed (in arbitrary units).

17. Of the following examples those marked (*) are taken from the preceding table.

Argon.

(Pure Argon.)

*	a .	.2.	.4.	.6.	.8.
q	22	58.5	161	550	
e	22	56.8	146	376	
E	22	58.3	163	550	

$X=190$. $p=2.55$. $\alpha=4.74$.
 $\beta=.0389$.

(Gas which has been in ionization-chamber one week.)

	a .	.2.	.4.	.6.	.8.	1.0.
q	12.5	28.2	69.0	180	600	
e	12.5	28.2	63.1	142	319	
E	12.5	28.5	68.0	178	509	

$X=204$. $p=2.55$. $\alpha=4.05$
 $\beta=.0363$.

(Pure Argon.)

*	a .	.1.	.2.	.3.	.4.	.5.
q	19.7	37.5	74	171	565	
e	19.7	35.9	66.3	120	219	
E	19.7	37.1	73.9	169	566	

$X=396$. $p=.638$. $\alpha=6.02$.
 $\beta=.220$.

(Gas which has stood 5 weeks.)

*	a .	.1.	.2.	.6.	.8.
q	18	25.5	126	380	
e	18	25.8	105	212	
E	18	25.9	127	380	

$X=229$. $p=.374$. $\alpha=3.52$.
 $\beta=.119$.

Hydrogen.

*	a .	.2.	.4.	.8.	1.0.
q	8.4	16.7	69	158	
e	8.4	16.7	65.3	130	
E	8.4	16.8	70.7	158	

$X=301.5$. $p=4.1$. $\alpha=2.42$.
 $\beta=.023$.

Nitrogen.

*	a .	.1.	.5.	.7.	.9.
q	13	64	161	420	
e	13	66	153	349	
E	13	67	150	420	

$X=410$. $p=2.48$. $\alpha=4.13$.
 $\beta=.0176$.

18. The following is a short summary of results obtained :—

I. *With Hydrogen and Nitrogen :*

1. The values obtained for both $\frac{\alpha}{p}$ and $\frac{\beta}{p}$ are in good agreement with those found by Townsend and Hurst.

2. For nitrogen, however, values of $\frac{\alpha}{p}$ are slightly higher than Hurst's in the range $\left(\frac{X}{p}\right) = 100$ to 350 ; whilst in the same range $\frac{\beta}{p}$ values are lower than his.

3. The effect of the electrons was observed for values of $\frac{X}{p}$ as low as 5 in hydrogen and 10 in nitrogen.

4. The effect of the positive ions was observed for values of $\frac{X}{p}$ as low as 30 for hydrogen, and 100 for nitrogen.

5. No evidence was obtained of any distinctive variation in the ionization due to *slight* contamination of these gases. The effect due to *larger* amounts of impurities has already been inquired into by the earlier investigators.

6. As the earlier work was done with brass and zinc electrodes, and the present with silver electrodes, the nature of the metal used seems to have no appreciable effect on the processes by which the currents increase with the distance between the plates.

II. *With Argon :*

1. There is a general agreement between the values of $\frac{\alpha}{p}$ and $\frac{\beta}{p}$ corresponding to the higher values of $\frac{X}{p}$ obtained in these experiments and those found by the earlier investigators.

2. The values of $\frac{\alpha}{p}$ and $\frac{\beta}{p}$ corresponding to the lower values of $\frac{X}{p}$ were larger than those previously obtained.

3. The effect of the electrons was observed for very small values of the ratio $\frac{X}{p}$, as low as 2.

4. The effect of the positive ions was measurable with pure gas down to $\frac{X}{p} = 10$; but with slight contamination it was not detected lower than $\frac{X}{p} = 20$.

5. In the region $\left(\frac{X}{p}\right) = 2$ to 10, the effect of the electrons may easily be reduced by impurities to one-fifth of its value with pure argon.

6. Comparatively low sparking-potentials were obtained, and it was found that impurities increased the sparking-potential.

19. I wish in conclusion to thank Professor Townsend, both for the specimen of carefully purified argon which he kindly supplied to me, and also for his constant sympathy and ready advice on all occasions.

XXXVII. *On certain Fundamental Principles of Scientific Inquiry. (Second Paper.)* By DOROTHY WRINCH, D.Sc., Fellow of Girton College and Member of the Research Staff, University College, London, and HAROLD JEFFREYS, M.A., D.Sc., Fellow of St. John's College, Cambridge*.

IT is a universal belief among physicists that when a sufficient number of inferences from a quantitative law have been verified, the probability of the correctness of the next inference from it may be made to approach indefinitely near to unity. It was shown in a former paper † that this proposition is not easily reconcilable with the other proposition, also believed by some physicists, that all laws of some infinite class are equally probable *à priori*; but that it is a necessary consequence of the contradictory proposition, which appears not unplausible, that the prior probabilities of admissible laws are not all equal, the simpler in fact having the higher probabilities. It was pointed out further that, if the admissible laws are all arranged in a series according to their probabilities, the current process of taking the simplest law that fits the facts can never enable one to proceed more than a finite number of steps along this series, and accordingly the laws capable of being discovered must form an

* Communicated by the Authors.

† Phil. Mag. xlii. pp. 369-390 (1921).

enumerable aggregate. In particular, since it appears that the constants in physical equations are often capable of continuous variation, or of discontinuous variation through more values than can be examined, we must suppose that laws containing such parameters are not in forms suitable for the comparison of their probabilities. They must have these parameters removed, by differentiation or otherwise, before such a comparison can be carried out. In particular, where a law can be expressed as a differential equation or as its integral, the latter involving one or more arbitrary constants, the latter cannot be the fundamental form of the law in our knowledge, while the differential equation may be. One consequence of the inadmissibility of quantities capable of discontinuous variation through more than a certain number of values is that the fundamental form of the law of gravitation cannot involve the mass of the attracting body explicitly. Thus the Newtonian form of it cannot be the fundamental one; nor can the Poisson form nor the equation in Einstein's system that corresponds to it, since the density occurs as a parameter in these and is capable of many values. On the other hand, the Laplace equation holding in regions containing no matter, or the corresponding Einstein equation

$$G_{\mu\nu}=0,$$

may be fundamental. This appears to be the decisive and unequivocal answer to the question, whether action takes place at a distance or by continuous transference: there is no question as to the truth or otherwise of the differential as against the integrated forms of the law of gravitation, since they in fact imply each other; but the differential form is more fundamental in knowledge since it sums up all possible forms of the integrated law. Again, the non-fundamental character of Poisson's equation and its analogue seems to require the density itself to satisfy a definite differential equation, which scarcely seems possible in view of the way we can vary it at will, or else that these equations are only macroscopic in character. The latter alternative would require that Laplace's equation or its analogue holds strictly at all points not within the ultimate particles of matter, and that the arbitrariness in the solution is supplied by the boundary conditions at the margins of these.

It was pointed out in the paper already referred to that laws differing slightly with regard to some fundamental constant must be in general widely separated in the series arranged

Phil. Mag. Ser. 6. Vol. 45. No. 266. Feb. 1923. 2 B

according to prior probabilities. If, for instance, the law involves only two terms, and in one possible law the constant considered is an integer, while in the other it differs from this integer by $1/n$, we showed that in one plausible arrangement these laws would be separated by something of the order of $\pi(n)$ terms, where π^* is the number of numbers less than n and prime to it.

It follows that the law established with a high probability by experience is never an approximation to the simple law, but the exact simple law itself. In other words, extrapolation over an indefinitely wide range can be carried out with the full probability of the law. This statement, however, requires further discussion. The data actually obtained by experiment are never such that they can *exactly* satisfy a quantitative law as they stand; they are of the form "the mark x lies between the n th and $(n+1)$ th marks on the scale" or "the sensation y occurred between the m th and $(m+1)$ th ticks of the clock after the last minute." There are two possible attitudes towards such measures. We can say either that they form a series of discrete values like n and m , only a few of which can possibly satisfy the law exactly; or that there is in each case a "true value" to which the measured value is only a rough approximation, and which does accurately satisfy the law. The latter alternative appears plausible at a first view, but is quite inadmissible as a part of knowledge. In the first place, as has been stated above, many of the quantities are involved through their differential coefficients, which are in no case directly measurable. Further, if it be once admitted that there is a true value which may be equal to any value in a certain compact series, so far as our prior knowledge can tell us, we must recognize that the number of possible true values that fit the law is infinite; for if the law connects x and y , say, there will be certain ranges of values of x and y such that every value of x within one corresponds to a value of y within the other, and *vice versa*. Thus the "true value" can in no case be determined uniquely from the knowledge at our disposal.

The solution of the difficulty appears to rest in a definite admission that the observations in fact do not as a rule satisfy the law. The fundamental data of all empirical knowledge

* It has been proved that $\pi(n)$ is asymptotically equivalent to $n/\log n$. For other properties of this function $\pi(n)$ reference should be made to the writings of Mertens, Hadamard, Von Mangoldt, De la Vallée-Poussin, Landau, Littlewood, and Hardy. References may be found in Landau's *Primzahlen* (Teubner, 1909).

are sensations ; those sensations involved in measurement form a large class of special interest for physics. The laws of physics are derived from measures, with the assistance of certain other principles of a non-logical character, the principle of simplicity being among the chief. They are therefore less fundamental in knowledge than the data of measurement.

Any observed measure is liable to differ slightly from the measure of the same quantity calculated by inference from the laws established. This is a matter of experimental fact ; and it is no violation of our principles that it should be so, for it is characteristic of quantitative inference that it only infers an observed value approximately and with a high degree of probability. It does infer that the observed value will lie within certain limits ; these are to be found as follows. If any measured quantity l_r is found to lie between n_r and $n_r + 1$ units, and another measure l_s is to be inferred from a number of such measures, we obtain the maximum limit by supposing each measure l_r to have the value n_r or $n_r + 1$ units, whichever gives the greater calculated value of the measure l_s to be inferred. By an analogous procedure we can find the lower limit of the inferred quantity, and our inference is strictly of the form that the observed measure will almost certainly lie within the limits thus obtained. In our subsequent work we shall not usually state our results in this form, but in the more compact one given by the simple law itself. Nevertheless, they can always be restated in the strict form by applying the above rules, and it is only when this has been done that verification has any meaning.

Inferences of this form are all that are ever made in science, and the characteristic feature, namely, a certain latitude in the verification, which we by convention call the margin of error, duly appears in the result. It follows by the argument in our former paper that if the law has a finite prior probability, we can by making a sufficient number of verifications make the probability of subsequent verifications approach indefinitely near to unity. Accordingly, this postulate is a sufficient explanation of the high probability usually attached to quantitative inference.

As has already been stated, it would be an error to consider that this result proves that scientific inference has a wholly logical basis. The theory we have developed links together a postulate which has been stated in formal terms *

* *Loc. cit.* pp. 378-9.

in the paper already quoted, and is summarized in the opening paragraph of the present paper, with the proposition, habitually assumed in science, that quantitative inference from the simplest law that fits the facts is reliable. It is, indeed, proved that the second is a logical consequence of the first. The denial of the first would make it extremely difficult to construct a theory that would include the second. The result therefore constitutes a contribution to scientific methodology, which aims at reducing the propositions habitually assumed in scientific investigations to groups of more fundamental propositions which imply them, and is not an attempt to prove that these fundamental propositions have themselves a basis in logic. The sole reasons for believing them are their intrinsic plausibility and the unplausibility of consequences deduced from their contradictories.

The structure of the theory of scientific method is strictly analogous to the structure of pure geometry, each consisting of a set of fundamental propositions with a logical superstructure. The main differences are that the fundamental propositions of science include facts of sensation, and that principles of probability inference, including empirical generalization, are employed in the development. Given all the fundamental propositions of scientific inference, the probability of any proposition whatever in science is determinate.

In practice, one is not interested only in the relation between the fundamental propositions and the inferences from them; for it is important to be in a position to assert the inferences without repeating the fundamental propositions every time. This will be accomplished only if the fundamental propositions are believed. We have indicated reasons for believing them, but we must repeat that this belief is at bottom not logical. The theory we are attempting to construct is one that includes the processes actually employed by scientific workers; since psychology is by definition the study of behaviour, this work may perhaps be regarded as a part of psychology. We think that the use of such a theory is to facilitate the understanding of the structure of physics, and thereby to suggest which methods of development and criticism are in closest accordance with the principles that are generally believed to lead to reliable results. For instance, one often hears the legitimacy of inference criticised in the case of new and unfamiliar laws, and it seems desirable that it should be pointed out that the

process of inference and the reason for believing the results are just the same in these cases as with laws that have been known much longer.

In addition to the known measured value of a physical quantity and the unknowable "true value" there may be a third quantity not found wholly by measure, and quite unique. This we shall call the "adopted value." This occurs when we have a number of observations of one or more variables, which have been found to be fitted approximately by one or more physical laws. The case of a single measurement carried out several times may be included under this head, the law involved being merely one of constancy with regard to the time. The observations will not in general fit the law exactly, and it may be useful to adopt some method of finding values near to them that do fit it exactly. The Method of Least Squares is one specially convenient method, but there are many others. It is a matter of convention which method we adopt, but when we have chosen one the values found by it are unique. These values are called the adopted values. They are evidently less fundamental in knowledge than the laws, and still less so than the measured values.

We have remarked already that the measurable values of a quantity form a discrete series containing an enumerable set of terms; hence its ordinal type is finite or ω . Irrational numbers form no part of the measurable values. On the other hand, the adopted values form a compact series. For, suppose a quantity to be measurable as either n or $n+1$ units. Then it is possible that after a number of measures have been made, r of them have been found equal to n and s to $n+1$. The adopted value, according to

the usual least square method, would be $n + \frac{s}{r+s}$. Now,

however short the interval between two numbers both less than 1 may be, there are always values of r and s such that $s/(r+s)$ lies between them. Hence there are possible adopted values of the quantity in every interval from n to $n+1$, and in general we may say that the possible adopted values form a compact series. On the other hand, the cardinal number of this series is only $\aleph_0$. For, the possible physical laws have number $\aleph_0$. Each has a finite number of integrals. These, with any conventional method of fitting, give in each case a single finite set or a finite number of finite sets of adopted values. Hence, by the method used to show that

the roots of all algebraic equations are of number $\aleph_0$, we may show that the possible adopted values have number $\aleph_0$. Hence the possible adopted values of any variable form a series of ordinal type η .

It is often desirable to express physical laws in forms involving only ratios of measures among themselves, and not a specified unit. An example of this procedure is to be found in the fundamental result used in our forthcoming development of mensuration. Each such ratio is the ratio of two terms, each of which may have any integral value in terms of the unit; hence the possible values of such ratios form a series of ordinal type η , the type of the rational fractions in order of magnitude. The special advantage of this method of expressing a law is, of course, that it remains completely unaltered when a change of units is made.

On the other hand, any continuum must have number $2^{\aleph_0}$. This introduces a theoretical difficulty. For it follows from the foregoing argument that no physical law in its integrated form can involve variables capable of more than $\aleph_0$ values, even if we include adopted values and ratios of measures. Hence continua have no place in physics; the closest type of series possible is η .

The ordinary discussions of differentiation cover cases of the differentiation of functions specified for all values of a continuous variable. Such specification, as we have already shown, is never possible in physics. It is sufficient for our purposes, however, to define differentiation in such a way that it can be applied to functions specified for only an η of values. In the case of functions specified only for a finite number of discrete values, the differential coefficients must be defined by the conventional process of interpolation; this is, indeed, how they are always found in practice.

XXXVIII. *The Calculation of the Magnetron Number of an Atom in Solution.* By J. H. SMITH, M.Sc., Assistant in Physics, University College, London*.

WEISS (*Le Radium* p. 8, 1911), using the numerical results of a large number of experimental measurements of the magnetic susceptibility of metals of the iron group and of their compounds, concluded that the magnetic moment of an atom of this group was always an integral multiple of an ultimate magnetic unit which he called the magneton.

The magnetic moment per gram molecule of a substance at absolute zero is calculated in the following way.

Let χ be the volume susceptibility at a temperature T° Abs. of a substance of density d and molecular weight M . The molecular susceptibility at T° is $M \frac{\chi}{d}$. Using Langevin's theory for a paramagnetic gas we have $\frac{I}{I_0} = \frac{I_0 H}{3RT}$, where I and I_0 are intensities of magnetization, H the external magnetic field in absolute C.G.S. units, and R is the gas constant 8.315×10^7 ergs.

The magnetic moment per gram molecule at absolute zero

$$= \sqrt{3RTM \frac{\chi}{d}}$$

In the case of solution the theory of Langevin for a paramagnetic gas is assumed to hold good. In general also Wiedemann's law that the magnetic susceptibilities are purely additive is also assumed. For solution of the chlorides, nitrates, and sulphates of the iron group in water, this has been verified by several workers. (A review of published work on the theory is given by Cabrera, *Journal de Chimie Physique*, xvi. 1918.)

The magnetic moment per gram atom for the metal is found by subtracting the diamagnetic moment per gram acid radicle (*i. e.* for Cl_2 , SO_4 , or NO_3) from the magnetic moment of the gram molecule found as above. The values of the diamagnetic moments of the acid radicles are taken from those deduced by Pascal (*Annales de Chimie et Physique*, xix. 1910) from measurements of magnetic susceptibility for series of organic compounds. These values are corrected to agree with the later determinations of the susceptibility of water, since Pascal made all his measurements using water

* Communicated by Prof. A. W. Porter, F.R.S.

as a standard. The accepted value was then $\cdot 75 \times 10^{-7}$; $\cdot 720 \times 10^{-7}$ is the mean value of the most recent determinations.

The magnitude of this correction is shown in the following example taken from the results of Weiss and Bruins (*Koninklijke Akademie van Wetenschappen te Amsterdam*, xviii. p. 1, 1915):—

Molecular susceptibility of nickel chloride $443\cdot6 \times 10^{-5}$

Atomic susceptibility of nickel at 18°C . $447\cdot6 \times 10^{-5}$

The correction for the Cl_2 radicle, $4\cdot0 \times 10^{-5}$, is seen to be about 1 per cent. For cobalt and iron salts the percentage correction is rather less.

In addition to so allowing for the Cl radicle there is a further correction of the same type which ought to be made; for in the molecule of nickel chloride there must be two systems with diamagnetic moments. The nickel atom itself must have a diamagnetic moment which is comparable with that of the Cl_2 radicle.

The typical atom of the iron group must consist of a nucleus and planetary system, in which the orbits of the outer electrons are mutually compensatory as regards the magnetic field produced by them at any external point, with the addition, characteristic of the group, of an uncompensated orbit. By an uncompensated orbit is meant one which can be rotated by external magnetic fields.

Let A be the centre of the uncompensated element of such an atom. Any other single electron in the atom, moving in a circular orbit with frequency n , will produce a magnetic field for which the magnetic vector at A can be written Gne —where G depends on the size of the orbit and the position of A with regard to it. Suppose that μ is the magnetic moment of the uncompensated element. Between the latter and the orbit considered there will be a relative magnetic energy $Gne\mu \cos \phi$, where ϕ is the angle between the axis of μ and the vector Gne . If $\sum Gne \cos \phi \mu$ be taken for all the orbits of the atom, the result will be zero if there is only one uncompensated orbit. But even if this is so, the orbits of the compensated type must have a diamagnetic moment which is comparable with that of the acid radicle. Thus all the values which have been calculated for the magnetic moments of the paramagnetic atoms must be smaller than the magnetic moment of the uncompensated element alone. The diamagnetic moment of the atom must also vary with the frequency of the electrons in compensated orbits, unless there is a change of area of orbit with frequency, such that the product of these two is constant.

Weiss and Bruins (*loc. cit.*) found that, when ammonia is added to solutions of nickel salts in water, the magneton number of nickel drops from 16.03 to 15.57, although Wiedemann's additive law is still obeyed. If the moment of the uncompensated orbit remains constant, then, on the addition of ammonia, there must be an increase in the diamagnetic moment of the nickel atom. The colour of the solution changes from green to brown, and this indicates a change of frequency of the electrons which are responsible for light-absorption. If measurements were made on the change of position of the absorption bands, characteristic of the nickel atom in solution, when the ammonia is added it might be possible to obtain some relation between the change of frequency and the increase of diamagnetic moment.

Since there was no apparatus available to investigate the colour change of the nickel solutions, it was decided to use instead cobalt chloride solutions in water and in absolute alcohol. The solutions of cobalt salts in water have a well-defined absorption maximum in the green, which moves towards the red end of the spectrum when the salts are dissolved in alcohol.

The positions of the maxima of these bands were investigated with a Hüfner spectrophotometer, as modified by Mees ('Photographic Journal,' July 1904).

In water solutions the absorption maximum was found to be at 0.510μ , and in the alcohol solutions at 0.65μ . These results are in good agreement with those obtained by Houstoun and Gray (Proc. R. S. Edinburgh, xxxi. p. 547), but differ from the positions estimated from series of photographs through solutions of different strengths by Jones and Anderson (Carnegie Publications 110).

The measurements of magnetic susceptibility were made with apparatus similar to that described by Pascal (*Annales de Chimie et Physique*, viii. p. 289, 1910). The method was first suggested by Kelvin. If the substance is obtained in the form of a uniform cylinder, and one end of the cylinder is situated in a field of strength H and the other end in a field of strength h , the cylinder experiences a force $\frac{1}{2}\chi(H^2 - h^2)S$, where S is the cross-section of the cylinder and χ is the apparent volume susceptibility of the substance, that is, the difference between its susceptibility and that of the surrounding medium. The force was measured by suspending a thin-walled glass tube containing the liquid from one arm of a balance, the base of the tube being situated between the poles of a large electromagnet, and finding the change in weight of the tube and contents when the current passes through the coils of the electromagnet.

The molecular susceptibility of the alcohol used was found, by comparison with water, to be 3.40×10^{-3} . The value found by Pascal (*loc. cit.*) was 3.43×10^{-3} , when corrected by the more recent value of the susceptibility of water.

The volume susceptibility of cobalt chloride in solutions of various strengths was found to be about 2 per cent. less in alcoholic solutions than in water solutions of the same strengths. The magneton number of cobalt in the water solutions, calculated by the method used by Weiss, was 24.6. Miss Brant ('Physical Review,' xvii. p. 678, 1921) found 24.5.

It is found therefore that, if the moment of the uncompensated element is constant, the diamagnetic moment of the molecule must increase, although the frequency of resonators corresponding to the absorption maximum is decreased. The areas of these orbits may change. It must also be remembered that they are probably only a part of the compensated system. A reasonable conclusion is that the frequency of the uncompensated element is diminished in the alcohol solutions, just as that of the light absorbers is diminished. The mass of evidence collected during recent years for the two paramagnetic gases (oxygen and nitrous oxide), for solutions, and for crystals shows that experimentally we find that neither the magneton of Weiss, nor that of Bohr, which is about five times the former, fits in with the experimental results.

The study of the variation of magnetic susceptibility with temperature in platinum and palladium has led Foëx (*Annales de Physique*, ix. p. 16, 1921) to conclude that these metals possess not only a diamagnetism which is independent of the temperature, but also a paramagnetic part to which he assigns the magneton number 8. It is evident that all atoms have a diamagnetic moment.

Westgren ('Journal of the Iron and Steel Institute,' May 1921) has shown that the crystal structure of iron does not change at the recalcrescence temperature, so that there can be considerable changes in the uncompensated orbits without any apparent change in the distribution of the outer electrons of the atom. A change in the distribution and frequency of the latter will, however, produce a change in the diamagnetic moment of the atom, as was shown by Oxley (*Phil. Trans. R. S.* 214. A. *et seq.*). Such changes account for the discontinuities observed by Theodoridès (*Comptes Rendus*, clxxi. p. 715, 1920), when he plotted $1/\chi$ against the absolute temperature for certain paramagnetic crystals.

XXXIX. *The Range of Alpha-Particles from Polonium in Various Gases.* By C. W. VAN DER MERWE, M.Sc.,
Lecturer in Physics, University of Cape Town*.

[Plate IV.]

THE Polonium which was the source of the α -rays in these experiments was kindly sent to me by Sir E. Rutherford through Mr. C. T. R. Wilson.

The range of the α -particles was determined by C. T. R. Wilson's† method of photographing the tracks in air saturated with water-vapour. Several improvements were made in the form of the apparatus. Wherever possible, brass was used in the construction instead of glass. A brass plate with a narrow horizontal slit, which was attached to the plunger, stopped the α -rays from traversing the cloud chamber, except at the end of the expansion when the slit was directly opposite the source of the α -rays.

Gelatine, which Wilson used for coating the inside of the cloud chamber, was found to be unsatisfactory because a fungus readily formed on it; but a jelly consisting of 6 parts by weight of glycerine (4 of water, 1 of gelatine, and 1 of sugar), proved satisfactory even at the higher temperature prevailing in Cape Town in the month of February.

Many photographs of the tracks in each gas were taken, and the maximum range on each plate was selected as being the range of the particle projected from the surface of the radioactive material in that particular experiment.

The initial temperatures and pressures were observed, and the final temperatures and pressures were calculated from the adiabatic expansion ratio.

The range in moist air was found to be 5.57 cm. at 258.1° K. and 462.2 mm. pressure, which corresponds to a range of 3.59 cm. at N.T.P. Geiger‡ found the range of α -particles from polonium by the ionization method to be 3.58 cm. at N.T.P., a highly satisfactory agreement between the two methods.

Since water-vapour is less dense than air, the range in

* Communicated by Sir W. H. Bragg, K.B.E., F.R.S.

† Wilson, Proc. Roy. Soc. A. lxxxv. p. 285 (1911).

‡ Geiger, Phil. Mag. Oct. 1911.

dry air should be less than that in air saturated with water-vapour; for, according to Sir W. H. Bragg*, the stopping-power of an atom is proportional to the square root of its atomic weight. An attempt was made to calculate the stopping-power of water-vapour relative to that of air from many determinations of the ranges in saturated air, assuming Geiger's value for dry air.

If m is the number of water-vapour molecules and n the number of air molecules, then the stopping-power of water-vapour is given by

$$\frac{ms+n}{m+n} = \frac{r_1}{r_2},$$

where r_1 is the range in dry air and r_2 is the range in moist air. Although these experiments gave a mean value of 0.77 as the stopping-power, while Bragg's formula gives 0.79, the method cannot be regarded as satisfactory for the purpose. The photographic tracks are faint near their ends, and therefore cannot be measured with the necessary accuracy, for r_2 is only slightly greater than r_1 . This faintness of the photographic tracks near their ends is explained by the experiments of Geiger† and G. H. Henderson‡, who showed that the ionization along the path of the particle does not suddenly stop. The ionization goes on increasing slightly until near the end of the path, and then falls off very rapidly.

The experiments, however, show that we may assume the stopping-power of water-vapour equal to 0.79 in correcting for the presence of water-vapour in other gases.

The following table exhibits the stopping-powers of several gases determined in this way, alongside the values calculated from Bragg's law, as well as the values for rays from Radium A and Radium C determined by Bragg and Kleeman§.

The greatest difference between the experimental and calculated values of the stopping-power is that of hydrogen. This is explained by the fact that the range in hydrogen was too long for the cloud chamber, and it was cut down by interposing aluminium foil, whose equivalent hydrogen path

* Bragg, 'Studies in Radioactivity,' p. 42.

† Geiger, Proc. Roy. Soc. lxxxii. p. 489.

‡ Henderson, Phil. Mag. Oct. 1921, p. 538.

§ Bragg & Kleeman, Phil. Mag. x. p. 318 (1905).

had to be calculated. The calculated range of hydrogen is probably too large. Pl. IV. shows a few specimen photographs of the tracks.

Stopping-Powers.

	Source of α -rays. Polonium.		Bragg's Experiments.		Range at N.T.P.
	exp.	cal.	Radium A.	Radium C.	cms.
Air	1.00	1.00	1.00	1.00	3.58
Hydrogen	0.22	0.26	—	0.24	16.28
Water-vapour	0.77	0.79			
Methane	0.91	0.98	0.88	0.86	3.96
Nitrogen	0.90	0.99	0.98	0.99	3.62
Carbon Monoxide ...	1.02	0.98	0.98	0.99	3.51
Oxygen	1.08	1.06	1.057	1.064	3.32
Nitric Oxide	1.11	1.02			3.23
Carbon Dioxide	1.52	1.51	1.49	1.51	2.36
Sulphur Dioxide ...	1.82	1.80			1.97
Methyl Bromide ...	2.04	2.08	2.03	2.09	1.76

Summary.

An experimental determination of the ranges of α -particles from Polonium, in several gases, by Wilson's photographic method proves that the stopping-powers of these gases may be calculated from Bragg's law.

I wish to express my appreciation of the interest taken in this work by Prof. A. Ogg and Dr. Lewis Simons, and also my indebtedness to Mr. J. A. Linton for the efficiency with which he constructed the apparatus used in the course of the research.

University of Cape Town,
September 1922.

XL. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from vol. xliv. p. 1062.]

November 8th, 1922.—Prof. A. C. Seward, Sc.D., F.R.S.,
President, in the Chair.

THE following communications were read:—

1. 'The Earthquake of 7th August, 1895, in Northern Italy.
By Richard Dixon Oldham, F.R.S., F.G.S.

This earthquake, although nowhere more than a feeble shock, was felt over an area measuring about 160 miles across and covering some 15,000 to 20,000 square miles in Lombardy and Tuscany. A detailed examination of the reports gives no indication of a central area of greatest intensity; reports indicating an intensity of IV (Mercalli scale) are scattered over the whole area up to the extreme limits; reports of sounds and of noticeable vertical movement are similarly distributed. The nature of the disturbance was different from that usual in slight earthquakes, and more akin to that noticed in the outer parts of the seismic area of great earthquakes. The reports are discussed, and the conclusion is drawn that the depth of the ultimate origin of the earthquake must have been of the order of 100 miles or more.

2. 'The Pamir Earthquake of 18th February, 1911.' By Richard Dixon Oldham, F.R.S., F.G.S.

This earthquake has been attributed to the fall of a very large landslip, which certainly accompanied it. As a surface-origin of a great earthquake, registered by distant seismographs, is contrary to the trend of our knowledge, the original records of this earthquake have been investigated. These show that it was felt over an area of about 250 miles in diameter, that the region included by the VIII° R.F. isoseist measured about 40 miles across, and that over the greater part of this area destruction was extreme, and the hillsides were seamed with landslips. For all this there must have been a common cause, which is to be found in the earthquake, and this could not have been due to the great landslip, for it lies on the extreme limit, and not near the centre, of the region of destructive violence. Aftershocks were recorded, providing further evidence that the earthquake was of the ordinary type, having its origin at a considerable depth below the surface. It is pointed out that the great landslip, though determined by, and not determining, the earthquake, may have influenced the distant seismograms by setting up surface-waves which, superimposed on those

directly due to the earthquake, may account for the unusual size of the long (or surface-) waves, as compared with the preliminary tremors.

3. 'The Geology of Sierra Leone.' By Frank Dixey, D.Sc., F.G.S.

About half of the Protectorate of Sierra Leone is composed of potash-bearing granites and granite-gneisses, while the remaining areas are occupied equally by older schists and gneisses and the ancient sedimentary Rokell River Series.

The older schists and gneisses, including a charnockitic series similar to that of the Ivory Coast, represent a complex of highly metamorphosed sedimentary and igneous rocks.

The normal granites and gneisses are associated with tourmaline-granites, cancrinite-syenite, alkaline gabbros, and a number of minor intrusions. Basic igneous rocks, of various ages, are represented by the great noritic complex of the Sierra Leone Peninsula, and by a large number of dolerite-dykes that cut the older crystalline rocks and also the horizontal sandstones of the Saonia Scarp Series (presumably of early Palaeozoic age).

The Rokell River Series has a lower conglomeratic division that rests unconformably upon the crystalline rocks. Its upper portion is composed of argillaceous and arenaceous sediments, with which are interbedded a series of acid and basic lavas and rhyolitic ashes and tuffs. The rocks of the Rokell River Series are usually much disturbed, and show every gradation from slight deformation to intense dynamic metamorphism.

The southern margin of the great series of horizontal sandstones of French Guinea forms, near the Anglo-French boundary of the Protectorate, the Saonia Scarp, and thus the formation within the Protectorate bears the name Saonia Scarp Series. It rests alike with striking unconformity upon the Rokell River Series and the crystalline rocks.

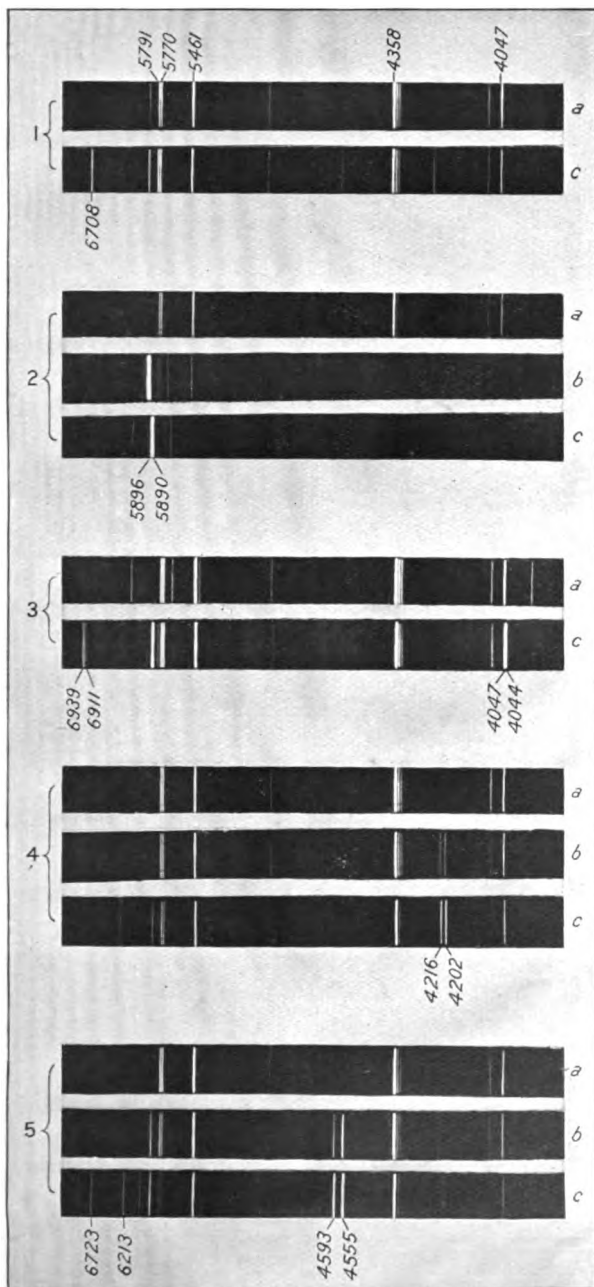
The Plateau Sands, resting upon the crystalline plateaux, are compared with the 'drift' of Northern Nigeria.

November 22nd, 1922.—Prof. A. C. Seward, Sc.D., F.R.S.,
President, in the Chair.

Prof. ARTHUR STANLEY EDDINGTON, M.A., F.R.S., Pres.R.A.S., delivered a lecture on *The Borderland of Astronomy and Geology*. He considered first, in reference to rival hypotheses as to the origin of the Earth and the solar system, the general evolution of the stellar universe. The trend of modern astronomy is against the view that luminous stars are being formed by collisions of extinct stars (unless very exceptionally); the stars now observed have systematic relations one to the other, apparently indicating that they have been formed as the result of a single

evolutionary process sweeping across the primordial matter. Collisions, in any case, would be extremely rare, since dynamical arguments indicate that extinct stars cannot greatly outnumber the observed luminous stars. Whether the original matter was gaseous or meteoric, it must have become entirely gaseous at a very early stage in the formation of a star: this is inferred from the fact that the masses of stars differ very little one from the other, and agree numerically with a certain critical mass, predicted theoretically for a sphere of gas, but unexplained if the star consisted of a swarm of meteorites. It is supposed that radiation-pressure was instrumental in breaking up the original matter into separate stars. These considerations favour the nebular hypothesis; but, if we accept Jeans's suggestion that the solar system is an exceptional formation, and that undisturbed stars cannot give birth to a planetary system, the argument is less cogent, since it refers only to stars developing normally. Astronomy now demands a great enlargement of Lord Kelvin's time-scale for the age of the sun; the most direct evidence is obtained from Cepheid variables, which are found to be developing at only 1/500 of the rate which Kelvin's hypothesis assumed. The sun must at one time have given out from 20 to 50 times as much heat as it emits now; but it is uncertain whether any geological strata go back to an epoch when the sun was sensibly hotter than now. Darwin's views on tidal evolution and the origin of the earth-moon system seem to have held their own against all criticism. The present rate of lengthening of the day (deduced from ancient eclipses) is about 1 minute in 6 million years; it is, therefore, difficult to date the birth of the moon later than 1000 million years ago. There seems to be no objection to the postulate that the Earth had a cool solid crust at the time of the catastrophe, if that would explain geological observations; the Pacific Ocean may be the depression which was left, and may have received the waters which formerly covered most of the Earth. The dissipation of energy by the tides occurs chiefly in the land-locked shallow seas, G. I. Taylor having shown that the Irish Sea alone accounts for 1/50 of the whole amount. The brake on the Earth's rotation is thus a surface-brake; and the hypothesis suggests itself that there may be a slip of the outer crust over the interior at the 'zone of weakness.' If the slip is irregular, this would help to explain certain astronomical observations of irregularities in the longitudes of the moon, sun, and planets. It might even be the cause of the motion of the magnetic poles. The brake, being applied irregularly over the surface, would also tend to crumple the crust. The postulated looseness of the crust might also permit the North Pole to move about over the surface; but exceedingly long periods of time would be required, since there is no systematic tendency of the crust to move in latitude.

**Spectra produced by an Electric Discharge through
a Mixture of Mercury and Alkali Metal vapours.**



1. Mercury and Lithium.
2. Mercury and Sodium.
3. Mercury and Potassium
4. Mercury and Rubidium.

- a. Condensed.
- b. Wehnelt Interrupter.
- c. Uncondensed.

VAN DER MERWE.

FIG. 1.

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

MARCH 1923.

XLI. *Precession of the Spinning Top.*
By Sir G. GREENHILL*.

[Plates V, VI, VII, VIII.]

SIGN and direction require careful consideration on a diagram of an actual case of top motion, and of the convention to be observed in the representation of a rotation by a vector, on the figure in Flatland.

In this representation the vector is assimilated to a screw, and taken in usual right-handed, for a rotation to give advance along the direction of the vector.

According as the top motion is mostly in the neighbourhood of the upright position and zenith of the top, or near the nadir and downward vertical, it is convenient to measure from the zenith or nadir the angle θ of inclination of the axle to the vertical, as in figs. A and B.

But in both cases the vector of the precession in azimuth, as well as OG, the vector of constant impulse about the vertical, is measured upward, as would be required in a Steady Motion.

Fig. 3, p. 182, *Phil. Mag.* July 1922, was not drawn with G above O, as it should have been on this plan, and so leads to some awkward change of sign; so too the references to a figure on p. 190 should be made to a figure A, with zenith θ .

On this right-handed screw system, the vector OC of the rotation of the Earth would be drawn from the centre to

* Communicated by the Author.

Phil. Mag. S. 6. Vol. 45. No. 267. March 1923. 2 C

the North Pole : such a rotation is called *deasil* in agriculture and *widdershins* if opposite, expressions familiar once to the ploughman and his team, in directing them to turn round.

Right and Left of the Sun are ancient expressions of doubtful meaning in direction, as we find in Herodotus and Xenophon. In his description of the voyage of circumnavigation of Lybia, sent out by Neco to sail down the Red Sea and return to Egypt by the Pillars of Hercules, Herodotus (iv. 42) declares his disbelief of the account brought back of the Sun being seen on the right hand, and we are left in doubt as to whether he means to the North or South, or if the equator was crossed.

After the battle of Cunaxa the Greeks are said by Xenophon to have marched away having the Sun on the right hand, and that would be to the East if marching North.

Aristotle (*de Cælo*) discusses a right and left hand of the Heavens, as of a living animal. In Esplandian, the enchanted island of California is placed to the Right of the Indies; and to day a Scot will give the direction "Turn to your East," meaning to the Right.

Turner has ignored the Right and Left hand of the sky in his picture where the Sun is shown setting in the East; so that Jonah's lament over Nineveh will hold today, of a city where they cannot discern between their right hand and the left.

Sitting in a room with the Sun on the right hand is awkward for writing, in throwing the shadow of the hand on the paper; much clearer to have the Sun on the left.

Fig. A and B are repeated here, drawn according to these conditions; and it will be noticed that a change from one to the other, from zenith to nadir θ , can be carried out in strict analogy by a mere change of θ into $\pi - \theta$, a change of $\cos \theta$ into $-\cos \theta$, z into $-z$, with a change of sign of $Q = \frac{d\theta}{dt}$, and of $\frac{dQ}{dt}$, leaving $\sin \theta$ unaltered.

In the discussion of Steady Motion, with constant precession μ , and its stability, as before in § 12, OA is drawn vertically upward on both figures to represent $\lambda = \frac{g}{\mu^2}$, the height of the conical pendulum AB to accompany the axle at its steady inclination to the vertical.

Then in our notation, with preponderance Ma , lb-ft, and transverse moment of inertia $A = MK^2$, lb-ft²,

$$OP = l = \frac{A}{Ma} = \frac{K^2}{a}, \text{ ft,}$$

is the S.E.P.L. of the top swinging as a pendulum in a

plane ; or if the top hangs down vertical at rest, and then rotates as a conical pendulum of small displacement with angular velocity n , $g=ln^2$, $gMa=An^2$; and it was proved (p. 191) that

$$L = \frac{g}{m^2} = \frac{OP^2}{AP^2} OA$$

is the S.E.P.L. to beat time with the slight nutation of the axle on its steady motion, corresponding to an apsidal angle

$$\mu \frac{\pi}{m} = \pi \frac{OP}{AP}.$$

Thus L is increased and the motion becomes more sluggish by making AP as small as possible, as in the upward vertical position; and if OP and OL are equal or nearly so, L becomes infinite or very large, and the motion is on the verge of instability.

On the diagram of fig. A, B, the length $l=OP$ fixes the scale of the other geometrical quantities, such as OA , a , K^2 , $\frac{A}{M}$, $\frac{C}{M}$.

But in the representation of the dynamical quantities, in OGKC, a length k is taken as the standard of the scale, and then with OG , $OC=\partial, \partial'$,

$$\frac{\partial, \partial'}{k} = \frac{G, CR}{2An} = \frac{h, k'}{n},$$

where $2An$ is the rotational impulse acquired by the top in falling about a horizontal axis from rest at the zenith through the nadir position (p. 181).

In accordance with previous notation (p. 190) and on fig. A, B, drawn to geometrical scale,

$$\frac{CK}{k} = \frac{A \sin \theta \frac{d\psi}{dt}}{2An}, \quad \frac{ON}{k} = \frac{A \frac{d\psi}{dt}}{2An}, \quad \dots \quad (1)$$

and with ϕ the hour angle,

$$R = \cos \theta \frac{d\psi}{dt} + \frac{d\phi}{dt},$$

$$\frac{A \frac{d\phi}{dt}}{2An} = \frac{CR - A \cos \theta \frac{d\psi}{dt}}{2An} = \frac{OC - MC}{k} = \frac{OM}{k}, \quad \dots \quad (2)$$

provided we take $A=C$, when the top is called spherical, a restriction on ϕ without influence on ψ , but making a

OGC of the paper, the dynamical equivalent of KH is $A \frac{d\theta}{dt}$, and on our right-handed system, HK is drawn away from the eye in fig. A, but towards us in fig. B.

It will save trouble in the statements if we ignore the distinction between a dynamical quantity and its geometrical representation, and treat them as equivalent in the equations; thus equating the velocity of H along KH to the impressed couple $An^2 \sin \theta$, and taking the radial component along GH,

$$\frac{dGH}{dt} = An^2 \sin \theta \cos GHK = An^2 \sin \theta \frac{HK}{GH}, \quad (3)$$

$$GH \frac{dGH}{dt} = A^2 n^2 \sin \theta \frac{d\theta}{dt}, \quad (4)$$

and integrating

$$GH^2 = 2A^2 n^2 (E - \cos \theta), \quad OH^2 = 2A^2 n^2 (F - \cos \theta), \\ CH^2 = 2A^2 n^2 (H - \cos \theta), \quad (5)$$

or to a geometrical scale again

$$GH^2 = \frac{1}{2} k^2 (E - z), \quad OH^2 = \frac{1}{2} k^2 (F - z), \\ CH^2 = \frac{1}{2} k^2 (H - z), \quad (6)$$

where E, F, H are dynamical constants, connected by

$$F = E + 2 \frac{h^2}{n^2} = H + 2 \frac{h'^2}{n^2}, \quad \text{or} \quad F = E + 2 \frac{\partial^2}{k^2} = H + 2 \frac{\partial'^2}{k^2}, \quad (7)$$

Again, resolving the velocity of H at right angles to GH, with (ρ, ϖ) the polar coordinates of H in the horizontal plane GHK,

$$\rho \frac{d\varpi}{dt} = An^2 \sin \theta \sin GHK \\ = An^2 \sin \theta \frac{GK}{GH} = An^2 \frac{OC - OG \cos \theta}{GH}, \quad (8)$$

$$\rho^2 \frac{d\varpi}{dt} = \frac{1}{2} kn (\partial' - \partial z), \quad \text{with} \quad \rho^2 = \frac{1}{2} k^2 (E - z), \quad (9)$$

with $\cos \theta = z$, equivalent to

Fig. A. $\frac{d\varpi}{dt} = \frac{h' - hz}{E - z}$		Fig. B. $\frac{d\varpi}{dt} = \frac{h' + hz}{E + z} \quad (10)$
---	--	--

The geometrical relation $GH^2 = HK^2 + KG^2$, replaced in dynamical units, becomes

$$2A^2n^2(E - \cos \theta) = A \left(\frac{d\theta}{dt} \right)^2 + \left(\frac{CR - G \cos \theta}{\sin \theta} \right)^2, \quad (11)$$

$$\begin{aligned} \left(\frac{dz}{dt} \right)^2 &= 2n^2(E - z)(1 - z^2) - 4(h' - hz)^2 \\ &= 2n^2(F - z)(1 - z^2) - 4(h'^2 - 2hh'z + h^2) \\ &= 2n^2(H - z)(1 - z^2) - 4(h - h'z)^2 = 2n^2Z, \end{aligned} \quad (12)$$

$$Z = z_1 - z \cdot z_2 - z \cdot z - z_3,$$

$$\infty > z_1 > 1, E, F, H > z_2 > z > z_3 > -1 > -\infty, \quad (13)$$

in the sequence, leading to the Elliptic Function solution

$$z = z_2 \operatorname{sn}^2 \frac{1}{2}mt + z_3 \operatorname{cn}^2 \frac{1}{2}mt, \quad m^2 = 2n^2(z_1 - z_3).$$

This is to zenith θ ; to the nadir θ , the sign of z must be altered, leaving the form of the equation unchanged.

But the further integration for ϖ , ψ , and ϕ introduces the Third Elliptic Integral, III. E. I.

This dynamical equation (11) may be interpreted as a combination of the Energy Principle with the constancy of component impulse G round the vertical and CR about the axle.

A vector treatment is given by W. C. Baker in the *Physical Review*, April 1922; W. F. Osgood, *Bulletin American Math. Society*, June-July 1921.

Fundamental Theorems of Dynamics can usually be presented in an incisive manner, shorter and more convincing than by reading into volumes of Victorian method, in analytical treatment by a procession of equations and approximation, and the use of Lagrange's method.

The dynamics of the top, spinning about a fixed point O , may be stated in two Propositions:—

A. The impulse vector OH describes a curve, in a horizontal plane in consequence of the constancy of the component impulse about the vertical; and the projection of the C.G. of the top on this horizontal plane describes the hodograph of the curve of H , turned back through a right angle.

This is true universally of any unsymmetrical top.

But if the top has uniaxial symmetry:

B. The curve of H is a Poincaré herpolhode, and the angular velocity about the axle is constant.

Proposition A and B will give the "Top in two moves"; and the motion is expressed by the elliptic function when the top has uniaxial symmetry.

But so far, for the general unsymmetrical top, the determination of the curve of H has defied Analysis.

In the general unsteady motion of the symmetrical top, the velocity of H imparted by the gravity couple $An^2 \sin \theta$ is along KH, and is equal to the rate of growth of $KH = A \frac{d\theta}{dt}$, together with the velocity of K carried round the vertical OG with angular velocity $\frac{d\psi}{dt}$; and with $\frac{d\theta}{dt} = Q$,

Fig. A.

$$\begin{aligned} An^2 \sin \theta &= A \frac{dQ}{dt} + GK \frac{d\psi}{dt} \\ &= A \frac{dQ}{dt} + \frac{GK \cdot KC}{A \sin \theta} \end{aligned}$$

$$\frac{dGK}{d\theta} = \frac{KC}{\sin \theta}, \quad \frac{dKC}{d\theta} = \frac{GK}{\sin \theta}$$

Fig. B.

$$\begin{aligned} An^2 \sin \theta &= -A \frac{dQ}{dt} + GK \frac{d\psi}{dt} \\ &= -A \frac{dQ}{dt} + \frac{GK \cdot KC}{A \sin \theta} \end{aligned} \quad (14)$$

$$\frac{dGK}{d\theta} = -\frac{KC}{\sin \theta}, \quad \frac{dKC}{d\theta} = -\frac{GK}{\sin \theta} \quad (15)$$

obvious geometrically on the figure.

Differentiating with respect to θ , with $d\theta = Qdt$,

$$\begin{aligned} \frac{1}{Q} \frac{d^2 Q}{dt^2} &= n^2 \cos \theta & \frac{1}{Q} \frac{d^2 Q}{dt^2} &= -n^2 \cos \theta \\ &= \frac{GK^2 + KC^2 - GK \cdot KC \cos \theta}{A^2 \sin^2 \theta} & &= \frac{GK^2 + KC^2 + GK \cdot KC \cos \theta}{A^2 \sin^2 \theta} \\ &= n^2 \cos \theta - \frac{GC^2 - 3GK \cdot KC \cos \theta}{A^2 \sin^2 \theta} & &= -n^2 \cos \theta - \frac{GC^2 + 3GK \cdot KC \cos \theta}{A^2 \sin^2 \theta} \\ &= \left(n^2 + \frac{3OM \cdot ON}{A^2} \right) \cos \theta - \frac{OK^2}{A^2} & &= -\left(n^2 + \frac{3OM \cdot ON}{A^2} \right) \cos \theta - \frac{OK^2}{A^2} \end{aligned} \quad (16)$$

exact equations.

In a state of Steady Motion in regular precession μ , Q and $\frac{dQ}{dt}$ are zero; H and K coincide, and the velocity of K is

$$\begin{aligned} An^2 \sin \theta &= \mu \cdot GK, \quad An^2 = \mu \cdot OM, \\ A^2 n^2 &= A \mu \cdot OM = ON \cdot OM, \quad \frac{ON}{OM} = \frac{A^2 n^2}{A^2 \mu^2} = \frac{n^2}{\mu^2} = l, \end{aligned}$$

with

$$l = \frac{g}{n^2} = OP, \quad \lambda = \frac{g}{\mu^2} = OA; \quad \text{and} \quad OM \cdot ON = \frac{1}{4} k^2,$$

to scale.

Greenhill on Precession

$$OK^2 = OM^2 - 2OM \cdot ON \cos \theta + ON^2 \quad (17)$$

$$\frac{OK^2}{A^2 n^2} = \frac{OM}{ON} - 2 \cos \theta + \frac{ON}{OM} = \frac{n^2}{\mu^2} - 2 \cos \theta + \frac{\mu^2}{n^2} \quad (18)$$

otion, $\frac{1}{Q} \frac{d^2 Q}{dt^2} = -m^2$, where

$$2 \cos \theta + \frac{\mu^2}{n^2} \frac{m^2}{n^2} = \frac{OK^2}{A^2 n^2} + 4 \cos \theta = \frac{n^2}{\mu^2} + 2 \cos \theta + \frac{\mu^2}{n^2} = \frac{\lambda}{l} + 2 \cos \theta + \frac{l}{\lambda} = \frac{AP^2}{OA \cdot OP} \quad (19)$$

thout approximation, showing that the appear in a small nutational velocity beating $m/2\pi$ times a second, with an ode to node, as stated above,

$$\Psi = \mu \frac{\pi}{m} = \pi \frac{OP}{AP}$$

in, the top can spin steadily upright in then in general steady motion

$$CR = \frac{An^2}{\mu} + A\mu \cos \theta, \text{ with } \cos \theta = 1, \quad (20)$$

the two independent circlings of the cal, adding up to the general epicycle op when spinning upright, asleep.

OA' in fig. A, to represent the two GO is produced down to P, making

$$\cos \theta, \text{ or } 2 \frac{OC}{k} = \frac{OS}{OP} + \frac{OP}{OS} \cos \theta,$$

f OA, OP on the horizontal through O, le.

tratic for OS geometrically, draw the at a depth $ON = OP \cos \theta$ below O, on OP in R; then RP produced will ne DE at a distance $OD = (\partial'/k)OP$ of a circle of radius RE, crossing the in S, S', with $OS + OS' = OD$,

$$R^2 = OR^2 = OP \cdot ON = OP^2 \cos \theta.$$

Then SA, S'A' at right angles to PS, PS' will cut off the length OA, OA'.

So, too, for a prolate solid, like a china egg, spun upright on a table, discussed in R.G.T. p. 273, we take in the notation there

$$l = \frac{g}{n^2} = \frac{\frac{A}{M} + z^2}{z - \rho}, \quad k = 2(z - \rho), \quad \frac{\partial}{k} = \frac{\frac{C}{M} + z\rho}{\frac{A}{M} + z^2} \cdot \frac{R}{2n},$$

in the equations of the top, with $\partial = k$ on the verge of stability, and then the energy is

$$\frac{CR^2}{2g} = \frac{2C \cdot \frac{A}{M} + z^2 \cdot z - \rho}{\left(\frac{C}{M} + z\rho\right)^2}, \quad \text{or} \quad \frac{2A(z - \rho)}{\frac{C}{M}} \text{ ft. lb.},$$

on a smooth table.

Spinning upright inside a cup-shaped cavity, of radius of curvature ρ' , replace $\frac{1}{\rho}$ by $\frac{1}{\rho} - \frac{1}{\rho'}$; and change the sign of ρ' if the body is spinning on a rounded summit.

But with $G = CR < 2An$, the upright position is unstable; the axle will leave the zenith and ultimately reach an inclination θ_3 , where

$$\cos \frac{1}{2}\theta_3 = \frac{h}{n} = \frac{CR}{2An}.$$

Then reckoning the time from this lower position,

$$\sin \frac{1}{2}\theta = \sin \frac{1}{2}\theta_3 \operatorname{sech} \frac{1}{2}mt, \quad m = 2n \sin \frac{1}{2}\theta_3; \quad (21)$$

so that after another infinite time the axle will reach the upright zenith position again.

And for the azimuth ψ ,

$$\begin{aligned} \psi - ht &= \cos^{-1} \frac{\cos \frac{1}{2}\theta_3}{\cos \frac{1}{2}\theta} = \tan^{-1} (\tan \frac{1}{2}\theta_3 \operatorname{th} \frac{1}{2}mt) \\ &= \frac{1}{2} \cos^{-1} \frac{1 + \cos \theta_3 \operatorname{ch} mt}{\operatorname{ch} mt - \cos \theta_3} = \frac{1}{2} \sin^{-1} \frac{\sin \theta_3 \operatorname{sh} mt}{\operatorname{ch} mt - \cos \theta_3}. \quad (22) \end{aligned}$$

a relation connecting true anomaly $2(\psi - ht)$ with hyperbolic excentric anomaly mt in an hyperbolic orbit of excentricity $\sec \theta_3$; also

$$\begin{aligned} \cos \frac{1}{2}\theta \cos (\psi - ht) &= \cos \frac{1}{2}\theta_3, \\ \cos \frac{1}{2}\theta \sin (\psi - ht) &= \sin \frac{1}{2}\theta_3 \operatorname{th} \frac{1}{2}mt. \quad (23) \end{aligned}$$

In the herpolhode curve (ρ, ϖ) described by the impulse vector OH, $E=1$, $\frac{d\varpi}{dt}=h=h'$, $\rho^2=GH^2=\frac{1}{2}k^2(1-\cos\theta)$,

$$\rho = k \sin \frac{1}{2}\theta = k \sin \frac{1}{2}\theta_3 \operatorname{sech}(\varpi \tan \frac{1}{2}\theta_3),$$

$$\rho \operatorname{ch}(\varpi \tan \frac{1}{2}\theta_3) = \partial \tan \frac{1}{2}\theta_3, \dots \dots \dots (24)$$

a curve circling round the origin G, and reaching it as an asymptotic point, a separating herpolhode.

If a tap is given while the top is spinning upright, the axle will pass periodically through the zenith ($z_2=1$), and describe a Rosette curve, so called by Klein; the H curve will then be enclosed between two circles, and will have cusps on the outer circle, pointing to G.

A tap in the nadir position will create another similar Rosette figure, and the curve of H will then have cusps pointing away from G on an inner circle, and here $z_2=-1$.

But these herpolhode H curves are of general elliptic character.

Thus in an upper Rosette,

$$\sin \frac{1}{2}\theta = \sin \frac{1}{2}\theta_2 \operatorname{cn} \frac{1}{2}mt, \quad h=h', \quad \kappa' = \sin \frac{1}{2}\theta_2 / \operatorname{sh} \frac{1}{2}\theta_1,$$

and in a lower Rosette, to nadir θ ,

$$\sin \frac{1}{2}\theta = \sin \frac{1}{2}\theta_2 \operatorname{sn} \frac{1}{2}mt; \quad h=-h', \quad \kappa' = \cos \frac{1}{2}\theta_2 / \operatorname{ch} \frac{1}{2}\theta_1;$$

and in an Intermediate curve, where $z_1=1$, and to zenith θ ,

$$\sin \frac{1}{2}\theta = \sin \frac{1}{2}\theta_2 \operatorname{dn} \frac{1}{2}mt, \quad h=h', \quad \kappa' = \sin \frac{1}{2}\theta_2 / \sin \frac{1}{2}\theta_3.$$

The axle will start from a cusp if $G=CR \cos \theta_2$, $h=h'z_2$, $H=z_2$, and will proceed to describe a curve to be identified as a gravity brachistochrone on the sphere.

In the special case given before on p. 183,

$$\theta_3 = \frac{1}{2}\pi, \quad \cos \theta_2 = \kappa, \quad \cos \theta = \cos \theta_2 \operatorname{sn}^2 \frac{1}{2}mt = \kappa \operatorname{sn}^2 \frac{1}{2}mt,$$

$$\tan(\psi - ht) = \sqrt{\frac{\cos \theta \cdot \cos \theta_2 - \cos \theta}{1 - \cos \theta_2 \cos \theta}}$$

$$= \frac{\kappa \operatorname{sn} \frac{1}{2}mt \operatorname{cn} \frac{1}{2}mt}{\operatorname{dn} \frac{1}{2}mt} = \sqrt{\frac{1 - \operatorname{dn} \frac{mt}{2}}{1 + \operatorname{dn} \frac{mt}{2}}},$$

$$\cos 2(\psi - ht) = \operatorname{dn} mt, \quad \psi = ht + \frac{1}{2} \cos^{-1}(\operatorname{dn} mt); \dots \dots (25)$$

$$\tan(\phi - h't) = \sqrt{\frac{\cos \theta \cdot 1 - \cos \theta_2 \cos \theta}{\cos \theta_2 - \cos \theta}}$$

$$= \frac{\operatorname{sn} \frac{1}{2}mt \operatorname{dn} \frac{1}{2}mt}{\operatorname{cn} \frac{1}{2}mt} = \sqrt{\frac{1 - \operatorname{cn} \frac{mt}{2}}{1 + \operatorname{cn} \frac{mt}{2}}},$$

$$\cos 2(\phi - h't) = \operatorname{cn} mt, \quad \phi = h't + \frac{1}{2} \operatorname{am} mt. \dots \dots (26)$$

In this case we can write the equations

$$(1 + \cos \theta) \exp(\phi + \psi - qt)i = \sqrt{(\sec \theta_2 - \cos \theta \cdot \cos \theta_2 - \cos \theta)} \\ + i(\sqrt{\sec \theta_2} + \sqrt{\cos \theta_2}) \sqrt{\cos \theta} = 2\alpha^2 e^{-qt}, \quad (27)$$

$$(1 - \cos \theta) \exp(\phi - \psi - q't)i = \sqrt{(\sec \theta_2 - \cos \theta \cdot \cos \theta_2 - \cos \theta)} \\ + i(\sqrt{\sec \theta_2} - \sqrt{\cos \theta_2}) \sqrt{\cos \theta} = 2\gamma^2 e^{-q't}, \quad (28)$$

$$q, q' = h \pm h' = n\sqrt{(2 \sec \theta_2)} \pm n\sqrt{(2 \cos \theta_2)}, \quad (29)$$

and so identify a special algebraical case of Klein's parameters $\alpha, \beta, \gamma, \delta$ of his Kreisel-Theorie, defined in terms of Euler's angles θ, ϕ, ψ by

$$\alpha = \cos \frac{1}{2} \theta \exp \frac{1}{2}(\phi + \psi)i, \quad \beta = i \sin \frac{1}{2} \theta \exp \frac{1}{2}(-\phi + \psi)i, \\ \gamma = i \sin \frac{1}{2} \theta \exp \frac{1}{2}(\phi - \psi)i, \quad \delta = \cos \frac{1}{2} \theta \exp \frac{1}{2}(-\phi + \psi)i, \\ \alpha\delta = \cos^2 \frac{1}{2} \theta, \quad \beta\gamma = -\sin^2 \frac{1}{2} \theta, \quad \alpha\delta - \beta\gamma = 1.$$

Generally in any cusp motion, the hour angle ϕ is non-elliptic,

$$\sin \theta \cos(\phi - h't) = \sqrt{(z_1 + z_3 \cdot z_2 - z)}, \\ \sin \theta \sin(\phi - h't) = \sqrt{(z_1 - z \cdot z - z_3)}, \quad (30)$$

$$\tan(\phi - h't) = \sqrt{\frac{z_1 - z \cdot z - z_3}{z_1 + z_3 \cdot z_2 - z}} = \sqrt{\frac{z_1 - z_3}{z_1 + z_3}} \cdot \frac{\operatorname{dn} \frac{1}{2} mt \operatorname{sn} \frac{1}{2} mt}{\operatorname{cn} \frac{1}{2} mt} \\ = \sqrt{\frac{z_1 - z_3}{z_1 + z_3}} \sqrt{\frac{1 - \operatorname{cn} mt}{1 + \operatorname{cn} mt}} = \sqrt{\frac{z_1 - z_3}{z_1 + z_3}} \tan\left(\frac{1}{2} \operatorname{am} mt\right), \quad (31)$$

connecting true anomaly $2(\phi - h't)$ with excentric anomaly $\operatorname{am} mt$ in an elliptic orbit of excentricity z_3/z_1 .

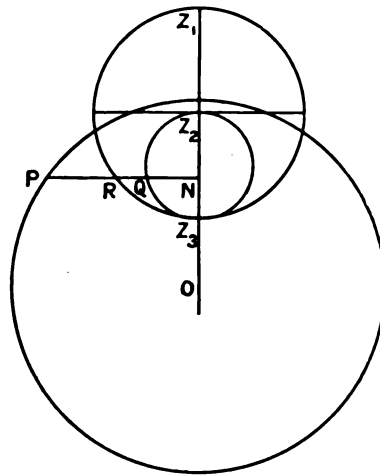
The brachistochrone cusp motion of the axle is rectifiable in the form

$$\cos \frac{s}{l} = \operatorname{dn} \frac{1}{2} mt = \sqrt{\frac{z_1 - z}{z_1 - z_3}}, \quad (32)$$

for s the length of the arc measured from the cusp described by the point P on the axle, $OP = l$.

Marking the points Z_1, Z_2, Z_3 on the vertical at height lz_1, lz_2, lz_3 above O , draw the circle on diameter Z_1Z_2 and Z_2Z_3 ; then if $PRQN$ is drawn horizontal, the arc s is $\frac{1}{2}l$ times the angle OZ_1R , in cusp motion.

Fig. 1.



And in the general top motion, the point P moves at the same level as R oscillating on the arc of the circle on Z_1Z_2 , below Z_2 , or as Q performing complete revolutions of the circle on Z_2Z_3 , each moving in a field of gravity of appropriate strength G in plane pendulum motion,

$$\frac{G}{g} = \left(\frac{z_1 - z_3}{z} \right)^2 \quad \text{or} \quad \left(\frac{z_2 - z_3}{z} \right)^2.$$

Any special curve in top motion is worth putting on record, an oasis in the desert of General Theory.

Great variety of pattern is obtainable, in the simple pseudo-elliptic cases above of ψ and ϕ , by the variation of the secular term ht or $h't$ at disposal.

But these curves are not algebraical, and to obtain an algebraical result the secular term must be cancelled; variety of pattern is then obtained by choosing an aliquot part of a period as the parameter of the III.E.I.; this has been developed in the Report on Gyroscopic Theory (R.G.T.), and shown here in Plates V, VI, VII, drawn by Sir George Hadcock, calculations by Col. R. L. Hippisley.

Thus for a bisection of the period, the algebraical result for ψ is of the form, to the nadir vertical (Plate V.)

$$\sin^2 \theta \cos 2\psi = (z + \frac{1}{2} \cdot z_1 + z_2) \sqrt{(z - z_1 \cdot z - z_2)},$$

$$\sin^2 \theta \sin 2\psi = R \sqrt{(2 \cdot z_3 - z)}, \quad . \quad . \quad . \quad . \quad . \quad (33)$$

$$z_3 = \frac{3 - 2\kappa + 3\kappa^2}{(1 + \kappa) \sqrt{(9 - 14\kappa + 9\kappa^2)}}, \quad z_2, z_1 = \frac{3 - 5\kappa, -5 + 3\kappa}{\sqrt{(9 - 14\kappa + 9\kappa^2)}},$$

$$R = \frac{4(1 - \kappa) \sqrt{(1 + \kappa)}}{(9 - 14\kappa + 9\kappa^2)^{\frac{1}{2}}}.$$

Introducing a Quadric Transformation, as in R.G.T. p. 121,

$$\kappa = \frac{1 - \gamma'}{1 + \gamma'}, \quad \sqrt{\kappa} \operatorname{sn} 2eK = \gamma \operatorname{sn} eG \operatorname{sn} (1 - e)G,$$

the result can be written

$$\frac{1}{2} M^2 \sin \theta e^{\psi i} = \frac{\gamma' \operatorname{cn} eG}{\gamma \operatorname{dn}^2 eG} + i \frac{\gamma' \operatorname{cn} (1 - e)G}{\gamma \operatorname{dn}^2 (1 - e)G},$$

$$\frac{1}{2} M^2 \gamma \theta' \sin \theta e^{\psi i} = \operatorname{cn} eG \operatorname{dn}^2 (1 - e)G + i \operatorname{cn} (1 - e)G \operatorname{dn} eG,$$

$$\frac{1}{2} M^2 \sin \theta_3 = \frac{\gamma'}{\gamma}, \quad M^2 = \frac{\sqrt{(1 + 8\gamma'^2)}}{\gamma^2},$$

$$\frac{\partial}{k} = \frac{\gamma'}{(1 + 8\gamma'^2)^{\frac{1}{2}}}, \quad \frac{\partial'}{k} = \frac{3\gamma'}{(1 + 8\gamma'^2)^{\frac{1}{2}}}; \quad . \quad . \quad (34)$$

and the herpolhode curve H of impulse is given in

$$M \frac{\rho}{k} e^{\varpi i} = \frac{\gamma' \rho}{\gamma \delta} = \operatorname{cn} eG + i \operatorname{cn} (1 - e)G, \quad . \quad . \quad (35)$$

with the time $t = eT$.

Set two pendulums swinging, to modulus γ , in perpendicular planes xOz , yOz , half a beat out of phase; with inclination a , b at time t ,

$$\tan \frac{1}{2}a = \frac{\gamma}{\gamma'} \operatorname{cn} eG, \quad \sin \frac{1}{2}a = \gamma \operatorname{sn} (1 - e)G, \quad \cos \frac{1}{2}a = \operatorname{dn} (1 - e)G,$$

$$\frac{\rho}{\delta} e^{\varpi i} = \tan \frac{1}{2}a + i \tan \frac{1}{2}b, \quad \sin \theta e^{\psi i} = \frac{\sin a + i \sin b}{\sqrt{(1 + 8\gamma'^2)}}.$$

If GM, GN are the coordinates of H in the invariable plane through G,

$$OM \cdot ON = \frac{\partial^2}{\gamma}, \quad \cos MON = \gamma',$$

MON is the modular angle of γ , and the rolling polhode curve is a plane hyperbola.

There will be cusps when $\gamma' = \frac{1}{2} = \cos 60^\circ$; and then

$$\kappa = \frac{1}{3}, \quad \theta_3 = 30^\circ, \quad \sec \theta_2 = \sqrt{3} = -z_1, \quad \frac{\partial, \partial'}{k} = \frac{1}{2\sqrt{3}}, \quad \frac{\sqrt[4]{3}}{2};$$

$$(\sin \theta e^{\psi i})^2 = (\cos \theta + \sec \theta_2)^{1/2} (\cos \theta - \cos \theta_3)^{3/2} \\ + i(\sec \theta_3)^{3/2} (\cos \theta_3 - \cos \theta)^{1/2}.$$

A figure is given (Plate VIII, and included in Plate V) of an algebraical four-fold gyroscopic motion, drawn by Sir George Hadcock, for modulus $\kappa = \sin 75^\circ$, $\gamma' = \cos 89^\circ$, with the dotted interior curve of impulse, the herpolhode of H; the other dotted part is the curve of P in the lower hemisphere.

An attempt is made to show with it a Pseudo-regular Precession in a curve of 40 small loops, drawn for a modular angle 10° of κ ; but the representation did not come out very distinct, as it is the projection of a looped curve on a steep part of the sphere; although seen sideways the loops are distinct and rounded and form a bold

flourish scroll, thus 

The curve was added also surrounding the figure as a necklace, a Regular Precession in 24 waves, going 7 times round, drawn for modular angle 1° of κ , as in a swift whirling of a spherical pendulum.

In a figure of a trisection of a period, an algebraical case of motion will be given by

$$(\sin \theta e^{\psi i})^3 \\ = (Qz + R) \sqrt{(z_1 - z)} + i(z^2 + Az + B) \sqrt{(z_2 - z)(z - z_3)} \\ \text{or} \\ (Qz + R) \sqrt{(z_2 - z)} + i(z_2 + Az + B) \sqrt{(z_1 - z)(z - z_3)}, \quad (36)$$

a curve in three or six loops (Plates VI, VII).

Thus with six cusps, and $z = \cos \theta$ to the nadir,

$$\kappa = \sin 15^\circ, \quad \theta_2 = 60^\circ, \quad \frac{\partial, \partial'}{k} = \frac{1}{2}, 1;$$

$$(\sin \theta e^{\psi i})^3 = (2z - 1)^{3/2} + i(1 - z + z^2) \sqrt{(2 - 2z - z^2)};$$

and with three cusps we find

$$\begin{aligned}\frac{\kappa}{\eta} &= 2 - \sqrt[3]{4} = \tan \theta_2 \sin \theta_3, \quad \sin \theta_3 = \sqrt[3]{4} - \sqrt[3]{2}, \\ \tan \theta_2 &= \sqrt[3]{2}, \quad z_1 = -\operatorname{ch} \theta_1, \quad \operatorname{sh} \theta_1 = \frac{1}{\sqrt[3]{2}}; \\ \frac{\partial, \partial'}{k} &= \frac{\sqrt{(\sqrt[3]{2}-1)}}{\sqrt[3]{4}} \left[\frac{1}{\sqrt[4]{(\sqrt[3]{4}+1)}}, \sqrt[4]{(\sqrt[3]{4}+1)} \right],\end{aligned}$$

from which the equation can be constructed.

And so on, for higher aliquot parts, as discussed in R.G.T.

To exterminate an approximation, and to replace it by an exact treatment of greater simplicity and conviction, this should be the object of modern procedure in the rediscussion of a familiar problem in former Theory.

Thus in our discussion of Small Oscillation in (19) on a state of Steady Motion the equations were exact, and the word *approximate* was banished as not conducive to conversion in the mind of a young Berkeley, devoted to Rigour of Argument.

XLII. On Tidal Stresses and Continental Displacements.

By H. H. POOLE, *Sc.D.* *

IN view of the very great interest which is at present being displayed in the question of continental displacements, it seems to be worth while to draw attention to the fact that, at the present day, the tangential stresses due to tidal action, whether oceanic or crustal, would appear to be absolutely incapable of causing appreciable horizontal motion in large land-masses. This has already been commented on by Dr. H. Jeffreys at the British Association Meeting at Hull†; but the following simple demonstration may be of interest.

Taking the mass of the Earth as 5.99×10^{27} grams, and its equatorial radius as 6.38×10^8 cm., we find that its moment of inertia (I) about its axis is 9.74×10^{44} gram sq. cm. Its angular velocity (ω) is about 7.29×10^{-5} radian per second.

Let us assume that in one century the day increases in length by 0.001 second. This figure has recently been

* Communicated by the Author.

† 'Nature,' Jan. 6, 1923, p. 31.

quoted by Prof. Eddington* as a probable measure of the retardation. It implies that each century is 36.5 seconds longer than the preceding one. The corresponding reduction in ω is given by the equation

$$-\frac{\delta\omega}{\omega} = \frac{0.001}{86,400} = 1.16 \times 10^{-8},$$

$$\therefore -\delta\omega = 8.45 \times 10^{-13};$$

since this occurs in 100 years

$$-\frac{d\omega}{dt} = \frac{8.45 \times 10^{-13}}{100 \times 365 \times 86,400} = 2.68 \times 10^{-22}.$$

$$\text{Hence loss of moment of momentum} = -I \frac{d\omega}{dt} = 2.6 \times 10^{23}$$

dyne cm. Now assume, as a first approximation, that the tangential stresses causing this retardation are uniformly distributed over the entire surface area, 5.1×10^{18} sq. cm. The average distance of the crust from the axis being 5.0×10^8 cm., the required stress would be

$$\frac{2.6 \times 10^{23}}{5.0 \times 10^8 \times 5.1 \times 10^{18}} = 1.02 \times 10^{-4} \text{ dyne per sq. cm.,}$$

i.e. only about one kilogram weight per square kilometre. This figure is so small that evidently, even if considerable concentration of the tangential forces on particular areas occurs, we should have to assume a rate of retardation quite incompatible with astronomical evidence, in order to account for the occurrence of stresses capable of causing appreciable relative movements involving distortion or fracture of the crust †.

It would seem then that, if tidal stresses have played a part in the history of the continents, they must have done so in past epochs, when, owing to crustal weakness or the closer proximity of the Moon, they were far more powerful than at present. This view accords well with the theory of continental displacement suggested by Dr. Joly in a forthcoming communication to the Royal Society.

Royal Dublin Society,
January 16, 1923.

* 'Nature,' Jan. 6, 1923, p. 20.

† So little is known of the sub-crustal conditions, that it appears to be conceivable that the minute stresses due to tidal action might cause a slow rotational motion of the crust as a whole relative to the interior, as has recently been suggested by Prof. Eddington. (Nature, loc. cit.)

XLIII. *On the Solution of the Representative Differential Equation of the Triode Oscillator.* By E. V. APPLETON, M.A., D.Sc., and W. M. H. GREAVES, M.A., St. John's College, Cambridge*.

AMONG the modern methods of producing sustained electrical oscillations that involving the use of a thermionic tube is by far the most flexible and convenient. Thus with a triode or dynatron oscillation generator a range of frequencies from 1 to 10^8 per second is now available for all kinds of physical investigations. In everyday wireless practice continuous-wave triode generators are gradually replacing the spark generators of Hertz and Marconi, and thus the theoretical problems of radio-telegraphic reception are being simplified in that the old problems of damped vibrations are being replaced by the simpler ones of undamped vibrations. But the simplification ends with reception, for the evolution of the continuous-wave generator has given rise to a whole series of theoretical problems which have not hitherto confronted the student of radio-telegraphy. Thus the linear equations of the older theory must now be replaced by the non-linear equations necessary for the representation of finite vibrations. The equations are non-linear because the assembly of any triode or dynatron generator may be reduced to a combination of an oscillatory circuit (capacity and self-induction), and a conductor (triode or dynatron) for which Ohm's law is not obeyed. A more detailed analysis shows that interest must now centre round the solution of the equation

$$\frac{d^2v}{dt^2} + f(v)\frac{dv}{dt} + \omega^2v = 0, \quad . \quad . \quad . \quad (1)$$

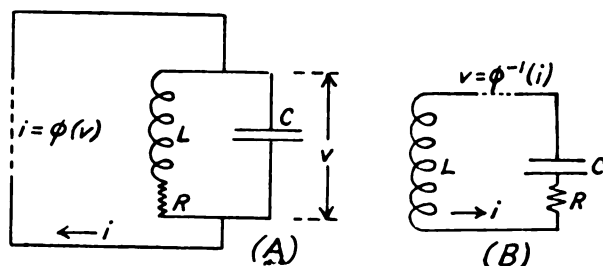
where v represents one of the variable electrical magnitudes (*e. g.*, current or potential difference), t the time, and ω is a constant. In the older equations the coefficient of $\frac{dv}{dt}$ is positive and constant, whereas in (1) the coefficient must be some function which assumes negative values for a certain range of values of v . In the simplest cases $f(v)$ is of the form $-\alpha + \gamma v^2$, where α and γ are positive constants. The amplitude of a generator represented by an equation of this type will automatically increase until a stationary value is

* Communicated by Sir J. Larmor, F.R.S.

reached. But often in practice $f(v)$ is of such a form (e. g., $\alpha - \gamma v^2 + \epsilon v^4$) that its value is positive when v is zero, but becomes negative when v is increased. In such cases oscillations will not start automatically, but if oscillations of amplitude greater than a certain critical value are temporarily induced in the system they are automatically maintained.

To illustrate the derivation of (1) and the determination of the appropriate values of the constants we may consider one or two examples. Almost all modern continuous-wave generators may be represented ideally by one of the two circuits shown in fig. 1, where the dotted lines represent some type of conductor not obeying Ohm's law and having a characteristic current-voltage relation expressed by $i = \phi(v)$, where i is the current through the conductor and v the difference of potential between its ends.

Fig. 1.



As examples of type A we may instance the ordinary triode and dynatron circuits, while the Duddell and Poulsen arcs are generators of type B. In both cases the relation between one of the variable electrical magnitudes and time t is represented by an equation exactly similar to (1). Thus in case A we may easily show that

$$\frac{d^2v}{dt^2} + \left[\frac{R}{L} + \frac{\phi'(v)}{C} \right] \frac{dv}{dt} + \frac{v}{CL} = 0^*.$$

* More precisely the equation for this circuit is

$$\frac{d^2v}{dt^2} + \left[\frac{R}{L} + \frac{\phi'(v)}{C} \right] \frac{dv}{dt} + \frac{v + Ri}{CL} = 0.$$

But in a practical case Ri is small compared with v . If, however, a case arose in which this were not so, the equation could still be treated in the same way. We have purposely not dealt with the more general equation so as not to make the algebra unduly complicated.

while in case B the analogous equation is

$$\frac{d^2 i}{dt^2} + \left[\frac{R}{L} + \frac{\frac{d}{di} \phi^{-1}(i)}{L} \right] \frac{di}{dt} + \frac{i}{CL} = 0.$$

From these equations it will be seen at once that the condition for instability in case A is that the coefficient of $\frac{dv}{dt}$ should be negative when $v=0$. Similarly in case B the coefficient of $\frac{di}{dt}$ should be negative when $i=0$. Thus in case A we must have

$$\frac{CR}{L} + \phi'(0) < 0,$$

and in case B

$$R + \frac{1}{\phi'(0)} < 0.$$

For instability in each case we must have a conductor with a falling current-voltage characteristic (*i. e.*, a so-called "negative resistance"). The derivation of a characteristic which illustrates the "negative resistance" effect of a triode oscillator has previously been given*. In the case of the arc the nature of the falling characteristic is well known.

In a recent paper † Dr. van der Pol and one of the writers gave an approximate solution of (1) which was, however, sufficiently accurate to account for the main features of the phenomenon of oscillation-hysteresis. In this approximate solution $f(v)$ was expressed as a power series, and use was made of the experimental fact, which is one quite familiar to practical workers, that the triode generator is singularly free from harmonics. Thus only the fundamental Fourier component of the current through the triode conductor was considered, the analysis being, in consequence, considerably simplified.

An elegant graphical solution of (1) has also been given by Dr. A. R. Robb ‡ for cases in which $f(v)$ is quite general. As, however, it is becoming more and more the custom in wireless practice to express the current-potential relations of

* Appleton & van der Pol, *Phil. Mag. Ser. 6*, vol. xlii. No. 248, p. 203, Aug. 1921.

† Appleton & van der Pol, "On a type of Oscillation-Hysteresis in a Simple Triode Generator," *Phil. Mag.* vol. xliii. p. 177, Jan. 1922.

‡ Robb, *Phil. Mag.* vol. xliii. p. 206, Jan. 1922.

triodes in the form of power series it seems desirable to treat (1) by purely analytical methods when $f(v)$ is expressed in this way, so that the amplitudes of the harmonics and the frequency of the generator can be accurately given. It is, in this way, possible to see what factors are responsible for the remarkably sinusoidal nature of the oscillation, and also to determine precisely the variation of the oscillation frequency with variation of the triode and circuit parameters. Experimental data on this latter point have been published recently*.

We are thus concerned with the equation

$$\frac{d^2v}{dt^2} + f(v) \frac{dv}{dt} + \omega^2 v = 0, \quad \dots \quad (1)$$

where $f(v)$ is a power series in v and may be written

$$f(v) = -\alpha + \beta v + \gamma v^2 + \delta v^3 + \epsilon v^4 + \dots, \quad \dots \quad (2)$$

the coefficients $\alpha, \beta, \gamma, \delta, \epsilon$, etc., being small compared with ω . We shall assume that the series (2) is convergent for all values of v which occur in practice. It is obvious that $v=0$ is a solution of (1). This solution corresponds to a "stationary state" of the system. We shall show that in addition to this there are other "stationary states" given by periodic solutions of (1).

In determining these periodic solutions we shall introduce the condition that $v=0$ when $t=0$. This simply amounts to a suitable choice of the origin of time.

Let us write

$$\omega^2 = \omega_0^2(1 + \mu b_1 + \mu^2 b_2 + \mu^3 b_3 + \dots + \mu^r b_r + \dots), \quad (3)$$

and

$$\left. \begin{aligned} \frac{\alpha}{\omega_0} &= a_0 \mu, \\ \frac{\beta}{\omega_0} &= a_1 \mu, \\ \frac{\gamma}{\omega_0} &= a_2 \mu, \\ \frac{\delta}{\omega_0} &= a_3 \mu, \\ \frac{\epsilon}{\omega_0} &= a_4 \mu, \quad \text{etc.} \end{aligned} \right\} \dots \dots \dots (4)$$

* Eccles & Vincent, Proc. Roy. Soc. 96 A. p. 455, Feb. 3rd, 1920; and Vincent, Proc. Roy. Soc. 97 A. p. 191, 1920: see also a paper by Miss Leyshon, 'Radio Review,' vol. i. No. 10, p. 481, July 1920.

where μ is small. Let also

$$\omega_0 t = \tau. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Thus, writing D for $\frac{d}{d\tau}$, (1) becomes

$$D^2 v + \mu(-a_0 + a_1 v + a_2 v^2 + a_3 v^3 + a_4 v^4 \dots + a_r v^r + \dots) Dv \\ + v(1 + \mu b_1 + \mu^2 b_2 + \dots + \mu^r b_r + \dots) = 0. \quad (6)$$

Let us assume as a solution

$$v = v_0 + v_1 \mu + v_2 \mu^2 + \dots + v_r \mu^r + \dots, \quad . \quad . \quad (7)$$

where v_0, v_1, v_2 , etc. are periodic functions of τ with period 2π , all of which are zero when $\tau=0$.

To determine v_0, v_1, v_2 , etc. we substitute the expression (7) for v in equation (6) and equate coefficients of like powers of μ .

From the terms in μ^0 we obtain

$$(D^2 + 1)v_0 = 0,$$

and therefore using the condition that $v_0=0$ when $\tau=0$ we have

$$v_0 = A \sin \tau, \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where A is a constant to be determined later.

From the terms in μ we obtain

$$(D^2 + 1)v_1 + P_1 = 0, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where

$$P_1 = L \frac{dv_0}{d\tau} + b_1 v_0, \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and

$$L = -a_0 + a_1 v_0 + a_2 v_0^2 + a_3 v_0^3 + a_4 v_0^4 + \dots + a_r v_0^r + \dots \quad (11)$$

We get from (8) and (11), writing $i = \sqrt{-1}$ as usual,

$$L = l_0 + l_1(e^{i\tau} - e^{-i\tau}) + l_2(e^{2i\tau} + e^{-2i\tau}) \\ + l_3(e^{3i\tau} - e^{-3i\tau}) + l_4(e^{4i\tau} + e^{-4i\tau}) \\ + \dots \\ + l_{2n}(e^{2ni\tau} + e^{-2ni\tau}) + l_{2n+1}(e^{(2n+1)i\tau} - e^{-(2n+1)i\tau}) \\ + \dots, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where

$$\left. \begin{aligned} l_0 &= -a_0 + \frac{1}{2}a_2A^2 + \frac{3}{8}a_4A^4 + \text{terms in } a_6A^6, a_8A^8, \text{ etc.}, \\ l_1 &= \frac{1}{2i} \left\{ a_1A + \frac{3}{4}a_3A^3 + \text{terms in } a_5A^5, a_7A^7, \text{ etc.}, \right\} \\ l_2 &= -\frac{1}{4}a_2A^2 - \frac{1}{4}a_4A^4 + \text{terms in } a_6A^6, a_8A^8, \text{ etc.}, \\ l_3 &= -\frac{1}{8i}a_3A^3 + \text{terms in } a_5A^5, a_7A^7, \text{ etc.}, \\ l_4 &= \frac{1}{16}a_4A^4 + \text{terms in } a_6A^6, a_8A^8, \text{ etc.}, \\ l_5 &= \text{terms in } a_5A^5, a_7A^7, \text{ etc.}, \\ l_6 &= \text{terms in } a_6A^6, a_8A^8, \text{ etc.}, \\ l_7 &= \text{terms in } a_7A^7, a_9A^9, \text{ etc.}, \end{aligned} \right\} \quad (13)$$

and generally

$$l_r = \text{terms in } a_rA^r, a_{r+2}A^{r+2}, a_{r+4}A^{r+4}, \text{ etc.}$$

Again, from (8),

$$\frac{dv_0}{d\tau} = \frac{1}{2}A(e^{i\tau} + e^{-i\tau}) \dots \dots \dots (14)$$

From (10), (12), and (14) we obtain

$$\begin{aligned} P_1 &= e^{i\tau} \left[\frac{1}{2}A(l_0 + l_2) + \frac{1}{2i}Ab_1 \right] + e^{-i\tau} \left[\frac{1}{2}A(l_0 + l_2) - \frac{1}{2i}Ab_1 \right] \\ &\quad + \frac{1}{2}A \sum_{n=1}^{\infty} \left[q_{2n}(e^{2ni\tau} - e^{-2ni\tau}) + q_{2n+1}(e^{(2n+1)i\tau} + e^{-(2n+1)i\tau}) \right], \end{aligned} \quad (15)$$

where we have written

$$l_{r-1} + l_{r+1} = q_r \dots \dots \dots (16)$$

In order that v_1 , as determined from (9) may be periodic in τ with period 2π , the coefficients of $e^{i\tau}$ and $e^{-i\tau}$ in the expression (15) for P_1 must be zero, so that we must have

$$b_1 = 0 \dots \dots \dots (17)$$

and

$$l_0 + l_2 = 0 \dots \dots \dots (18)$$

The equation (18) determines the constant A .

Equation (15) now becomes

$$P_1 = \frac{1}{2} A \sum_{n=1}^{\infty} \left[q_{2n} (e^{2ni\tau} - e^{-2ni\tau}) + q_{2n+1} (e^{(2n+1)i\tau} + e^{-(2n+1)i\tau}) \right], \quad (15')$$

and (9) gives

$$v_1 = \alpha_1 e^{i\tau} + \beta_1 e^{-i\tau} + \frac{1}{2} A \sum_{n=1}^{\infty} \left[\frac{q_{2n}}{(2n)^2 - 1} (e^{2ni\tau} - e^{-2ni\tau}) + \frac{q_{2n+1}}{(2n+1)^2 + 1} (e^{(2n+1)i\tau} + e^{-(2n+1)i\tau}) \right]. \quad (19)$$

where α_1 and β_1 are constants which are arbitrary so far.

We may also write (19)

$$v_1 = (\alpha_1 + \beta_1) \cos \tau + i(\alpha_1 - \beta_1) \sin \tau + \frac{1}{2} A \sum_{n=1}^{\infty} \left[\frac{2q_{2n}i}{(2n)^2 - 1} \sin 2n\tau + \frac{2q_{2n+1}}{(2n+1)^2 - 1} \cos (2n+1)\tau \right]. \quad (19')$$

From the terms in μ^2 we obtain

$$(D^2 + 1)v_2 + P_2 = 0, \quad (20)$$

where

$$P_2 = (-a_0 + a_1 v_0 + a_2 v_0^2 + \dots + a_r v_0^r + \dots) \frac{dv_1}{d\tau} + (a_1 v_1 + 2a_2 v_0 v_1 + 3a_3 v_0^2 v_1 + \dots + a_r v_0^{r-1} v_1 + \dots) \frac{dv_0}{d\tau} + b_2 v_0,$$

giving

$$P_2 = \frac{d}{d\tau} (L v_1) + b_2 v_0. \quad (21)$$

P_2 is a periodic function of τ with period 2π and may be written

$$P_2 = \sum_{r=-\infty}^{r=+\infty} P_{2,r} e^{ri\tau}. \quad (22)$$

For v_2 as determined by (20) to be periodic in τ with period 2π we must have

$$\left. \begin{aligned} P_{2,1} &= 0, \\ \text{and } P_{2,-1} &= 0. \end{aligned} \right\} \quad (23)$$

From (12) and (19) we find (using (16) and (18)) that in

$v_1 L$ the coefficients of $e^{i\tau}$ and $e^{-i\tau}$ are respectively,

$$l_0(\alpha_1 - \beta_1) - \frac{1}{2} A \sum_{n=2}^{\infty} \left[\frac{(-1)^n (q_n)^2}{n^2 - 1} \right]$$

$$\text{and } -l_0(\alpha_1 - \beta_1) - \frac{1}{2} A \sum_{n=2}^{\infty} \left[\frac{(-1)^n (q_n)^2}{n^2 - 1} \right].$$

We thus get

$$\left. \begin{aligned} P_{2,1} &= il_0(\alpha_1 - \beta_1) - \frac{1}{2} i A \sum_{n=2}^{\infty} \left[\frac{(-1)^n (q_n)^2}{n^2 - 1} \right] + \frac{1}{2i} b_2 A, \\ P_{2,-1} &= il_0(\alpha_1 - \beta_1) + \frac{1}{2} i A \sum_{n=2}^{\infty} \left[\frac{(-1)^n (q_n)^2}{n^2 - 1} \right] - \frac{1}{2i} b_2 A, \end{aligned} \right\} \quad (24)$$

and equations (23) become

$$\left. \begin{aligned} l_0(\alpha_1 - \beta_1) - \frac{1}{2} A \sum_{n=2}^{\infty} \left[\frac{(-1)^n (q_n)^2}{n^2 - 1} \right] - \frac{1}{2} b_2 A &= 0, \\ l_0(\alpha_1 - \beta_1) + \frac{1}{2} A \sum_{n=2}^{\infty} \left[\frac{(-1)^n (q_n)^2}{n^2 - 1} \right] + \frac{1}{2} b_2 A &= 0, \end{aligned} \right\} \quad (25)$$

giving

$$b_2 = - \sum_{n=2}^{\infty} \left[\frac{(-1)^n (q_n)^2}{n^2 - 1} \right] \quad . \quad . \quad . \quad (26)$$

and

$$\alpha_1 - \beta_1 = 0. \quad . \quad . \quad . \quad (27)$$

We now get from (19')

$$\begin{aligned} v_1 &= (\alpha_1 + \beta_1) \cos \tau + \frac{1}{2} A \sum_{n=1}^{\infty} \left[\frac{2q_{2n}i}{(2n)^2 - 1} \sin 2n\tau \right. \\ &\quad \left. + \frac{2q_{2n+1}}{(2n+1)^2 - 1} \cos (2n+1)\tau \right], \quad (19'') \end{aligned}$$

and choosing $(\alpha_1 + \beta_1)$, such that $v_1 = 0$ when $\tau = 0$, we get

$$\begin{aligned} v_1 &= -A \sum_{n=1}^{\infty} \left[\frac{q_{2n+1}}{(2n+1)^2 - 1} \right] \cos \tau \\ &\quad + A \sum_{n=1}^{\infty} \left[\frac{q_{2n}i}{(2n)^2 - 1} \sin 2n\tau + \frac{q_{2n+1}}{(2n+1)^2 - 1} \cos (2n+1)\tau \right]. \end{aligned} \quad . \quad . \quad . \quad (28)$$

We now get from (20)

$$v_2 = \alpha_2 e^{i\tau} + \beta_2 e^{-i\tau} + \sum_{r=-\infty}^{r=+\infty} \left(\frac{P_{2r} e^{ir\tau}}{r^2 - 1} \right),$$

where α_2 and β_2 are constants, arbitrary so far, which will be determined when we come to the consideration of the terms in μ^3 .

In general, we get from the terms in μ^n ,

$$v_n = \alpha_n e^{i\tau} + \beta_n e^{-i\tau} + \sum_{r=-\infty}^{r=+\infty} \frac{P_{nr}}{r^2 - 1} e^{ri\tau}, \quad \dots \quad (29)$$

where $P_{n,1}$ and $P_{n,-1}$ are zero.

The equation from which v_{n+1} is determined is

$$(D^2 + 1)v_{n+1} + P_{n+1} = 0, \quad \dots \quad (30)$$

where

$$\begin{aligned} P_{n+1} &= (-a_0 + a_1 v_0 + a_2 v_0^2 + \dots + a_r v_0^r + \dots) \frac{dv_n}{d\tau} \\ &\quad + (a_1 v_n + 2a_2 v_0 v_n + 3a_3 v_0^2 v_n + \dots + r a_r v_0^{r-1} v_n + \dots) \frac{dv_0}{d\tau} \\ &\quad + b_{n+1} v_0 + P_{n+1}^{(1)} \\ &= \frac{d}{d\tau} (L v_n) + v_0 b_{n+1} + P_{n+1}^{(1)}. \end{aligned}$$

Here $P_{n+1}^{(1)}$ is an expression not involving v_n or b_{n+1} and may be determined from the previous stages of the work.

P_{n+1} is a periodic function of τ with period 2π and may written

$$P_{n+1} = \sum_{r=-\infty}^{r=+\infty} P_{n+1,r} e^{ri\tau}.$$

Since v_{n+1} as determined from (30) is to be periodic in τ with period 2π we must have

$$\begin{aligned} P_{n+1,1} &= 0 \\ \text{and} \quad P_{n+1,-1} &= 0, \end{aligned}$$

giving

$$\begin{aligned} l_0(\alpha_n - \beta_n) - \frac{1}{2}b_{n+1}A + R_n &= 0, \\ l_0(\alpha_n + \beta_n) + \frac{1}{2}b_{n+1}A + S_n &= 0, \end{aligned}$$

where R_n and S_n are expressions not involving α_n , β_n and b_{n+1} , and which are determined from the results of the previous stages of the work. These equations determine b_{n+1} and $(\alpha_n - \beta_n)$. $(\alpha_n + \beta_n)$ is then determined by using the conditions that $v_n = 0$ when $\tau = 0$.

We have now shown how periodic solutions of (1) may be obtained, there being one such solution for every value of A which satisfies (18).

It should be noted that we have not demonstrated the convergence of the series obtained. These series are power series in μ , and it is reasonable to assume * that they will be convergent for sufficiently small values of μ , and therefore for sufficiently small values of $\frac{\alpha}{\omega}$, $\frac{\beta}{\omega}$, $\frac{\gamma}{\omega}$, etc.

To obtain a convenient approximate result, let us neglect the terms in μ^2 and higher powers of μ in the expression (7) for v , and the terms in μ^3 and higher powers of μ in the expression (3) for ω^2 .

We then have

$$v = v_0 + \mu v_1,$$

$$\omega^2 = \omega_0^2(1 + \mu^2 b_2).$$

In a practical case † it will often suffice to neglect all the coefficients in (2) except α and γ , in which case we have

$$f(v) = -\alpha + \gamma v^2. \quad \dots \quad (31)$$

Thus (18) becomes

$$-a_0 + \frac{1}{4}a_2 A^2 = 0,$$

giving

$$A = 2\sqrt{\frac{\alpha}{\gamma}}.$$

(28) becomes

$$v_1 = \frac{1}{8}a_0\sqrt{\frac{\alpha}{\gamma}}\cos\tau - \frac{1}{8}a_0\sqrt{\frac{\alpha}{\gamma}}\cos 3\tau,$$

and (26) becomes

$$b_2 = \frac{1}{8}a_0^2.$$

Thus the (approximate) solution is

$$v = 2\sqrt{\frac{\alpha}{\gamma}}\sin\omega_0 t + \frac{1}{8}\frac{\alpha}{\omega_0}\sqrt{\frac{\alpha}{\gamma}}\cos\omega_0 t - \frac{1}{8}\frac{\alpha}{\omega_0}\sqrt{\frac{\alpha}{\gamma}}\cos 3\omega_0 t, \quad \left. \begin{array}{l} \text{where } \omega_0 \text{ is given by} \\ \omega_0^2 = \omega^2 - \frac{1}{8}\alpha^2. \end{array} \right\} \quad \dots \quad (32)$$

It is sometimes ‡ desirable, however, to retain all the coefficients up to ϵ in (2) so that

$$f(v) = -\alpha + \beta v + \gamma v^2 + \delta v^3 + \epsilon v^4. \quad \dots \quad (33)$$

* This will be proved in a subsequent paper.

† Appleton & van der Pol, *loc. cit.* p. 182.

‡ Appleton & van der Pol, *loc. cit.* p. 183.

In this case (18) becomes

$$\epsilon A^4 + 2\gamma A^2 - 8\alpha = 0,$$

giving

$$A = \sqrt{-\frac{\gamma}{\epsilon}} \quad \sqrt{\frac{\gamma^2}{\epsilon^2} + \frac{8\alpha}{\epsilon}} \dots \dots \dots (34)$$

Corresponding to each of these two values of A there is a periodic solution. In this case we have

$$q_2 = \frac{1}{2i} \left(a_1 A + \frac{1}{2} a_3 A^3 \right),$$

$$q_3 = -\frac{1}{4} a_2 A^2 - \frac{3}{16} a_4 A^4,$$

$$q_4 = -\frac{1}{8i} a_3 A^3,$$

$$q_5 = \frac{1}{16} a_4 A^4,$$

$$q_6 = q_7 = q_8 = \dots = 0,$$

(28) becomes

$$\begin{aligned} r_1 = & A \left[\frac{1}{32} a_2 A^2 + \frac{1}{48} a_4 A^4 \right] \cos \tau \\ & + \frac{1}{6} A \left(a_1 A + \frac{1}{2} a_3 A^3 \right) \sin 2\tau - \frac{1}{32} A \left(a_2 + \frac{3}{4} a_4 A^2 \right) \cos 3\tau \\ & - \frac{1}{120} a_3 A^4 \sin 4\tau + \frac{1}{384} a_4 A^5 \cos 5\tau, \end{aligned}$$

and (26) becomes

$$\begin{aligned} b_2 = & \frac{1}{12} \left(a_1 A + \frac{1}{2} a_3 A^3 \right)^2 + \frac{1}{128} \left(a_2 A^2 + \frac{3}{4} a_4 A^4 \right)^2 \\ & + \frac{1}{960} a_3^2 A^6 + \frac{1}{6144} a_4^2 A^8, \end{aligned}$$

412 Dr. Appleton and Mr. Greaves : *Solution of the*
so that the (approximate) solutions are

$$\left. \begin{aligned} v = & A \sin \omega_0 t + \frac{1}{16} A \left(\frac{1}{2} \frac{\gamma}{\omega_0} A^2 + \frac{1}{3} \frac{\epsilon}{\omega_0} A^4 \right) \cos \omega_0 t \\ & + \frac{1}{6} A \left(\frac{\beta}{\omega_0} A + \frac{1}{2} \frac{\delta}{\omega_0} A^3 \right) \sin 2\omega_0 t \\ & - \frac{1}{32} A \left(\frac{\gamma}{\omega_0} + \frac{3}{4} \frac{\epsilon}{\omega_0} A^4 \right) \cos 3\omega_0 t \\ & - \frac{1}{120} \frac{\delta}{\omega_0} A^4 \sin 4\omega_0 t + \frac{1}{384} \frac{\epsilon}{\omega_0} A^5 \cos 5\omega_0 t, \end{aligned} \right\} (32')$$

where ω_0 is given by

$$\omega_0^2 = \omega^2 - \frac{1}{12} \left(\beta A + \frac{1}{2} \delta A^3 \right)^2 - \frac{1}{128} \left(\gamma A^3 + \frac{3}{4} \epsilon A^4 \right)^2 - \frac{1}{960} \delta^2 A^6 - \frac{1}{6144} \epsilon^2 A^8,$$

and A has either of the values (34).

We have previously seen that A is determined by the equation

$$l_0 + l_2 = 0,$$

and it is easy to see further that the general terms in the expressions for l_0 and l_2 are respectively

$$\frac{1}{2^{2n}} \frac{2n}{(n)^2} a_{2n} A^{2n},$$

and

$$- \frac{1}{2^{2n}} \frac{2n}{(n-1)(n+1)} a_{2n} A^{2n}.$$

The equation $l_0 + l_2 = 0$ thus becomes

$$-a_0 + \sum_{n=1}^{n=\infty} \frac{2n}{2^{2n}} \frac{a_{2n} A^{2n}}{n(n+1)} = 0. \quad \dots (35)$$

This is an equation determining A , and to every root there corresponds a periodic solution of (1) representing a "stationary state."

The condition for stability of these periodic solutions has been given in a previous paper*. It is (in the present notation)

$$-a_0 + \sum_{n=1}^{n=\infty} \frac{2n}{2^{2n}} \frac{a_{2n} A^{2n}}{(n)^2} > 0. \quad \dots (36)$$

* Appleton & van der Pol, *loc. cit.*, equation (10), p. 182.

Equations (32'), (34), and (36) therefore give us the information we require in practice regarding the amplitude, stability, and frequency of the oscillation in any stationary state. Equation (32') also enables us to determine the magnitude of the harmonics in any particular case.

Much experimental work has recently been carried out using the triode oscillator as a reference standard of frequency, and it is of interest to note that the variation of frequency with the triode parameters found in practice is in excellent agreement with that suggested by (32'). Thus the frequency is always found to be less than ω , the difference increasing as the amplitude A is increased.

It is also possible* to realize physically three of the "stationary states" indicated by the solution given above, of which one is given by $A = 0$ and the others by (34). Such "stationary states" are utilized in the so-called "trigger" relays, in which a transient signal causes the oscillator to pass from the "stationary state" $A=0$ to that of the first value of (34). The second value of A in (34), which represents an unstable "stationary state," may be identified with the so-called "threshold" value of the signal oscillation necessary for the relay to function.

Note (1).—It is of interest to notice that we can easily construct (mathematically at any rate) examples in which the equation (35) has an enumerable infinity of real roots. For instance, we may take

$$\begin{aligned} f(v) &= -\mu \cos v \dagger, \\ \text{so that} \quad & \left. \begin{aligned} a_0 &= 1, \\ a_{2n} &= \frac{(-1)^{n+1}}{(2n)!}, \quad (n > 0) \\ a_{2n+1} &= 0. \end{aligned} \right\} \end{aligned}$$

If we multiply (35) by $\frac{1}{2}A$ it becomes

$$\sum_{n=0}^{\infty} \frac{(-1)^{n+1} A^{2n+1}}{2^{2n+1} (n+1)!} = 0,$$

that is

$$J_1(A) = 0,$$

where, as usual, J_1 denotes the Bessel function of order 1.

* Appleton & van der Pol, *loc. cit.*

† This example arose out of a suggestion made by Mr. D. P. Dalzell, of St. John's College, Cambridge.

It is well known that this equation has an enumerable infinity of real roots.

Furthermore with these values of the a 's (36) becomes

$$1 + \sum_{n=1}^{n=\infty} \frac{(-1)^n A^{2n}}{2^{2n} (n)^2} < 0,$$

that is

$$J_0(A) < 0.$$

It is well known that $J_0(A)=0$ has an enumerable infinity of real roots, and that between every two of these there lies one, and only one, root of $J_1(A)=0$, so that the periodic solutions in this case are alternately stable and unstable.

This example suggests the possibility of the existence of physical systems, governed by the ordinary laws of Newtonian Mechanics, and possessing an enumerable infinity of alternately stable and unstable stationary states.

Note (2).—In the above work we have been concerned with the determination of the periodic solutions of (1) which give the stationary states of the system. These solutions are of mathematical interest as they are of a type rather different from the periodic solutions of dynamical equations which have been discussed by Poincaré. Their relation to the ordinary theory of periodic solutions will be discussed in a later paper.

We wish to express our gratitude to Professor Sir Joseph Larmor and Professor H. F. Baker for the kind interest they have taken in the preparation of this paper.

XLIV. *On Restricted Movements of Molecules at very low pressures.*

To the Editors of the Philosophical Magazine.

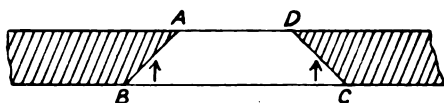
GENTLEMEN,—

IN the June *Philosophical Magazine*, under the title "Restricted Movements of Molecules at very low pressures," Arthur Fairbourne very interestingly sets forth a method for the possible experimental demonstration of a limit of applicability of the Second Law of Thermodynamics. In this paper, however, he seems to have overlooked a possibility of great importance for the mechanical realization of this aim. Fairbourne shows that tapered vessels, open at both ends, whose dimensions are made smaller than the free path of many of the molecules of the gas employed, may be expected to cause an appreciable flow of gas emerging from

the larger end of the vessel. He further proposes the mounting of a small vane within or below this opening for the detection of the expected motion in low-pressure gases.

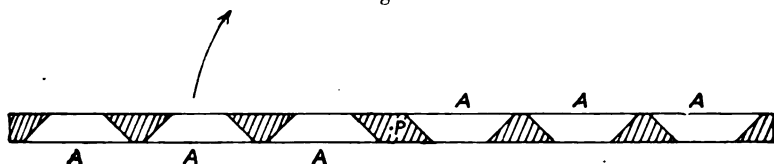
Since the flow in the gas is entirely the result of impacts of individual gas molecules against the walls of the vessel, it follows that there must result a corresponding reaction against the vessel itself opposite in direction to the gas-flow. That is, a pressure having an unbalanced component in the direction of the small opening must be exerted against the inner walls of the vessel. Let us attach this vessel to a flat plate so that it becomes a tapered aperture through the plate, as in fig. 1, instead of an independent vessel.

Fig. 1.



Evidently if we mount the plate as a vane suspended by a quartz fibre or other sufficiently delicate pivot, we should be able to detect a motion of the plate. The effect may be greatly multiplied by perforating the plate with a large number of tapered apertures, arranged as shown at A, A in fig. 2. If a vane of this type were delicately suspended in a

Fig. 2.



closed gas-filled vessel and the pressure gradually reduced, we should finally reach a point where the molecule paths have grown in length until the selective action becomes appreciable. Then we may expect the vane to start rotating about the pivot P in the direction of the arrow, and to maintain this motion at the expense of the heat in the gas so long as the necessary conditions are present. Obviously this apparatus is capable of far greater delicacy than is Fairbourne's suggested vane, which could utilize a portion only of the force resulting from a single aperture.

Yours faithfully,

HAVILAND H. PLATT.

Scarsdale, N.Y.

August 25th, 1922.

XLV. *The Specific Heats of Nitrous and Nitric Oxides.* By Prof. J. R. PARTINGTON, D.Sc., and W. G. SHILLING, M.C., M.Sc.*

THE following investigation was undertaken with the object of providing reasonably accurate data for the values of the specific heats of nitrous oxide and of nitric oxide. Nitrous oxide is of special interest from the standpoint of the Lewis-Langmuir theory when compared with carbon dioxide, since the two gases have identical external electronic structures. Their respective physical constants have, in very many cases, almost identical values. Nitric oxide is similar to carbon monoxide and to nitrogen, but the analogy is not so complete as in the case of nitrous oxide and carbon dioxide. This is only to be expected, since nitrogen and carbon monoxide have ten electrons in the outer shell, whereas nitric oxide has eleven.

The results previously obtained for nitrous oxide are so discordant that it is impossible to deduce any mean value from them. The differences may be largely attributed to the impurity of the gas used. Masson† determined the ratio of the specific heats by determining the frequencies with which a reed vibrated in the different gases. His observed value for nitrous oxide was $\kappa=1.28132$. A value of $\kappa=1.285$ was obtained by Cazin‡. He employed the adiabatic expansion method, using as the containing vessel a large globe of 60 litres capacity. Regnault§ measured the specific heat at constant pressure by his calorimeter method. He obtained a value, at 105° C. of ($p=9.94$ gm. cals. Employing Berthelot's equation of state, this leads to a value $\kappa=1.253$. Although Regnault estimated the amount of nitrogen present as an impurity, he did not consider his results as being very accurate. A method similar in principle to that afterwards used by Masson was employed by Dulong||. Assuming the velocity of sound in free air at 22° C. to be 333 m./sec., he found a value $\kappa=1.343$. His experimental figures, when recalculated using Berthelot's equation and modern physical constants, give $\kappa=1.332$. A value of $\kappa=1.3106$ for nitrous

* Communicated by the Authors.

† *Ann. de Chim. et de Phys.* (3) liii. p. 257 (1858).

‡ *Ann. de Chim. et de Phys.* lxxvi. p. 206 (1862); cf. *Phil. Mag.* (4) xl. p. 209 (1870).

§ *Mém. de l'Académie*, vol. xxvi. p. 135 (1862).

|| *Ann. de Chim. et de Phys.* (2) xli. p. 113 (1892).

oxide was obtained by Wüllner * by the dust-figure method. The above value, after a small correction for frequency and for inaccurate density values employed by Wüllner, gives $\kappa=1.323$. The only modern figures are those of Mercer, Schweikert, and those given by Heuse. Mercer † employed a platinum resistance thermometer to measure the instantaneous fall of temperature corresponding to a rapid fall of pressure. His apparatus was similar to that of Makower ‡, except that he used a very small vessel. He attempted to correct for the large influence which conduction and convection would have in this case. A correction was also applied for the 2.6 per cent. of oxygen in the nitrous oxide. This was assumed to be present as air (i. e. 13 per cent. impurity), and the correction was made by means of an equation which, as Stevens § had already shown, does not hold good experimentally. The above corrections, together with one for a defective thermometer, increased Mercer's observed value of κ for nitrous oxide from 1.229 to 1.261, a result which appears somewhat uncertain owing to the number and magnitude of the corrections necessary. Schweikert || reverted to a slight modification of the original Kundt method. His results give $\kappa=1.289$ at 0° C. The most recent result is that of Heuse ¶, who employed the constant-flow calorimeter method of Callendar and Barnes. This method appears always to give results for κ which are somewhat lower than those obtained by other methods **. The value for nitrous oxide given by Heuse is $\kappa=1.277$ at 0° C.

It will be seen that the above results, varying from $\kappa=1.25$ to $\kappa=1.32$, leave much doubt as to the correct value.

In the experiments described below, the method employed was that of Kundt as modified by Behn and Geiger. The method has been described in a recent paper ††, so that a reference to the modifications introduced will be sufficient. The gas-tube was now fitted with a side tube attached centrally to it and carrying a tap and one-half of a ground-glass joint. This side tube had no effect on the

* Wied. *Ann.* iv. p. 321 (1878).

† Proc. Phys. Soc. Lond. xxvi. p. 155 (1914).

‡ Phil. Mag., Feb. 1903.

§ Diss. Heidelberg, 1900.

|| *Ann. Phys.* (4) xlviii. p. 593 (1915).

¶ *Ann. Phys.* (4) lix. p. 86 (1919).

** Partington, Proc. Roy. Soc. A, vol. c. p. 47. (1921).

†† Partington & Cant, Phil. Mag. (6) xliii. p. 369 (1922).

vibration of the tube, since it passed through a slot cut in the wooden clamp. The great advantages of this fitting are that it is easily connected to the filling apparatus and the tube can be emptied and refilled as often as desired without cleaning and redrying; its ends can also be blown perfectly hemispherical. In the case of nitrous oxide the heat used in sealing-off would have decomposed some of the gas, had the previous method of closing the tube been used. Nitrous oxide begins to decompose at $520^{\circ}\text{C}.$ *, and the decomposition is complete at $900^{\circ}\text{C}.$ †. The tap attached to the side tube had a specially large bore of 4 mm. to facilitate washing and cleaning, and the barrel was sealed in with wax during actual use to prevent the possibility of its shaking loose by the vibration of the tube. The diagram of the apparatus (fig. 1) shows the complete arrangement.

Nearly all previous work on nitrous oxide has been vitiated by the use of impure gas. No account seems to have been taken of the fact that the gas made by heating ammonium nitrate inevitably contains nitrogen‡, the percentage of which varies from 2 per cent. upwards, according to the care taken in heating the ammonium nitrate. Reliquifying the gas in liquid air and allowing the nitrogen to boil off§ seems to be the only satisfactory method of eliminating this impurity. The commercial liquid which is stored at a pressure of 70–75 atmospheres, in cylinders, will contain this nitrogen in solution.

In the first series of experiments the technical gas from a cylinder was used. It was washed in solutions of ferrous sulphate and of potassium hydroxide. The nitrogen present was estimated by dissolving out the nitrous oxide in air-free water at $2^{\circ}\text{C}.$ after the experiment. Pure nitrous oxide was used in all other experiments. It was made|| by allowing a concentrated solution of sodium nitrite in air-free water to drop on to a solution of hydroxylamine hydrochloride also in air-free water. The generating apparatus, which could be completely evacuated, is shown on the left of fig. 1. The gas was passed through a 50 per cent. solution of sodium hydroxide and then dried by means of

* Berthelot, *C. R.* lxxvii. p. 1451 (1873).

† Meyer and Langen, *Pyrochem. Untersuch.* Brunswick, p. 65 (1885).

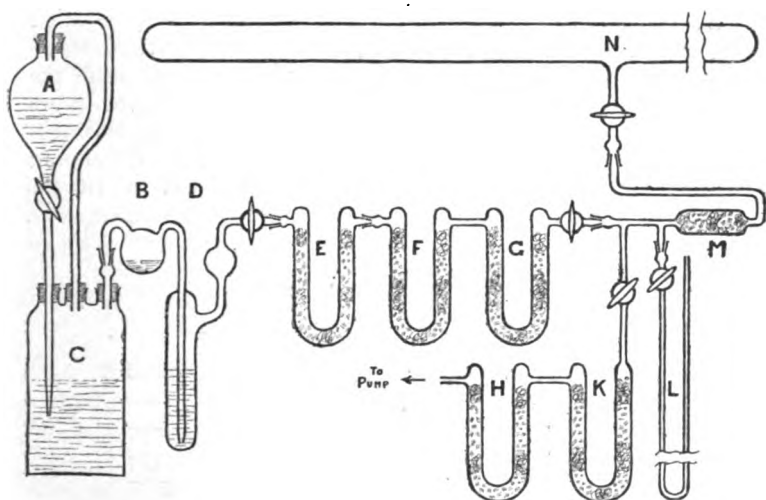
‡ Regnault, *Mém. de l'Acad.* vol. xxvi. p. 135 (1862); confirmed by Saunders, *J. C. S.* p. 698 (1922).

§ Villard, *C. R.* cxviii. p. 1096 (1894).

|| Meyer, *Wied. Ann.* clxxv. p. 141 (1875).

calcium chloride and phosphorus pentoxide. The whole apparatus was made to hold a vacuum for several hours previous to filling the tubes, thus ensuring the absence of any leakage. When the gas-tube was filled with a pure specimen of the gas, the tap was simply closed and sealed in with wax. The tube was then ready for the experiment.

Fig. 1.



A contains sodium nitrite solution for nitrous oxide, potassium ferrocyanide, and potassium nitrite solutions for nitric oxide; B is a trap for any liquid sucked back from D; C contains hydroxylamine hydrochloride solution for nitrous oxide, dilute acetic acid for nitric oxide; D contains 50 per cent. potassium hydroxide solution to eliminate any traces of chlorine, carbon dioxide, etc.; E is a calcium-chloride drying-tube for nitrous oxide, solid potassium hydroxide for nitric oxide; F and G are phosphorus pentoxide drying-tubes; L is the manometer; M a phosphorus pentoxide drying-tube; and N is the gas-tube.

Effect of moisture in the air in the comparison tube.

The value of κ for air which was used as the standard was taken to be 1.403 *. This value applies to dry air, free from carbon dioxide. Keutel† had found that the

* Partington, Proc. Roy. Soc. A, vol. c. (1921).

† Inaug. Diss. Berlin (1910).

error introduced by the use of ordinary air as the standard was negligible. It was, however, thought desirable to test this point. A series of experiments was therefore undertaken to compare the wave-lengths obtained in "pure" and in ordinary air. The results showed clearly that it is necessary, under the conditions obtaining in our laboratory, to take pure air as the standard.

In the first series of experiments, waves were produced and measured in the open air-tube filled with ordinary air. Air, purified by forcing it slowly over broken stick potassium hydroxide followed by two drying-tubes containing phosphorus pentoxide, was then passed into the air-tube for a period of 6 to 8 hours. Dust-figures were then produced in the fresh powder which had been introduced along the tube. The temperature remained constant throughout. Table I. gives the results obtained. In the first of the series the relative humidity was not measured.

TABLE I.

Wave-lengths in Dry and Moist Air.

Date.	Moist air.	Dry air.	Temp., ° C.	Humidity.
18.1.22	7.244	7.201	15.6	—
20.1.22	7.233	7.201	15.4	—
23.1.22	5.840	5.819	12.4	—
24.1.22	5.822	5.814	13.2	—
25.1.22	5.849	5.829	15.5	0.78
30.1.22	8.259	8.188	11.5	0.798
31.1.22	8.286	8.188	11.5	0.776
2.2.22	8.308	8.255	12.0	0.85 chem. method.
6.2.22	Identical waves.		7.0	0.38 " "
14.2.22	9.016	9.015	12.0	0.58 " "

Measurements of the humidity were taken by the chemical method for the last three of the series. The wet- and dry-bulb readings are only comparable under standard conditions and are of little use for this type of work. The more expeditious method of keeping a sealed tube filled with pure air was afterwards substituted for the somewhat tedious method described above. The ratio $(vel. \text{ in dry air}) / (vel. \text{ in moist air})$ was determined for the conditions of each experiment with other gases. By this method the wave-lengths in nitrous and nitric oxides were compared with that of pure dry air for every experiment.

The difference obtained by using pure air usually altered the value of κ by amounts which were certainly greater than the limits of error of the experiment.

Stevens* attempted to correct the value of C_p/C_v for moist air by a simple proportion on the ratio C_p/C_v for each of the gases concerned. But this could only be done if both gases were ideal. A simple proportion on C_v would be more accurate. The quantitative relations for gas mixtures have, unfortunately, not yet been investigated. Work in this direction will shortly be undertaken in this laboratory. Schweikert† deduced a formula for reducing values in moist air at $t^\circ \text{C.}$ to dry air at 0°C. But the formula holds only if C_p/C_v can be assumed to be constant for any temperature or gas mixture. This assumption is wrong theoretically and is not substantiated by any of the experimental evidence so far available. Since the experimental data at present available are not sufficient to test any formula which might be deduced, the method of correction by direct experiment, as described, was used throughout the present work.

Experimental Results.

Table II. gives the results obtained for nitrous oxide. Each experiment was carried out with a fresh sample of the pure gas, and the wave-lengths given are the mean values from a series of measurements. The first result is from a sample of the commercial gas from a cylinder. The nitrogen contained in it was estimated, as described, after the experiment, and a correction made on the value of C_v . The corrected value of the mean wave-length for this experiment has been calculated from the corrected value of C_v . A mean content of 8 per cent. of nitrogen was found. Tables III. to V. give a complete set of measurements for one experiment. In these tables the first column gives the number of half wave-lengths measured. The distances given under the headings A and B are the distances A'D', A'E', A'F', and BE, BF, etc. given in the lower diagram of fig. 2 in the paper of Partington and Cant already mentioned. Where two or three sets of readings are given, the zero was changed for the second and third sets.

* Diss. Heidelberg, 1900, pp. 29 *et seq.*

† *Ann. Phys.* xlviii. p. 598 (1914).

TABLE II.

Wave-lengths in Air and Nitrous Oxide.

Tube 1.

No. of exp.	Dry air. $\lambda/2$ corr.	N ₂ O. $\lambda/2$.	κ' .	ϕ .	κ .	Temp., ° C.
1.	7.775	6.023	1.279	1.0121	1.294	12.8
2.	7.052	5.471	1.283	1.0120	1.298	13.5
3.	7.053	5.461	1.278	1.0121	1.293	13.2
4.	6.752	5.234	1.280	1.0122	1.296	12.2
5.	6.750	5.232	1.280	1.0121	1.295	12.8
6.	7.050	5.475	1.286	1.0121	1.301	12.8
Means...	7.072	5.483	1.281	1.0121	1.296	12.9

Tube 2.

1.	8.155	6.308	—	—	—	11.5
2.	8.224	6.361	—	—	—	12.0
3.	8.690	6.690	—	—	—	11.2
Means...	8.356	6.453	1.272	1.0122	1.287	11.6

The discrepancy between tubes 1 and 2 in Table II. is explained later. The value of ϕ , the correction for the deviation of the gas from the ideal state, was calculated from Berthelot's equation, as in the paper of Partington and Cant.

TABLE III.

Series of Measurements for one Determination.
Temp. 13°·5 C.

To find the ratio Dry air/Moist air.

1. Dry air in sealed tube :— (all in cms.)

No.	A.	B.	Mean.	$\lambda/2$.
5.	{ 24.9 25.0	25 25.2	25.025	5.005
6.	{ 30.0 30.0	30.1 30.2	30.075	5.012
7.	{ 35.0 35.1	35.1 35.1	35.075	5.011
8.	{ 40.05 40.0	40.1 40.1	40.062	5.008
9.	{ 44.9 44.9	45.0 45.1	44.975	4.997
10.	{ 49.8 49.9	50.0 50.0	49.925	4.992
11.	{ 55.0 55.0	54.9 55.0	54.975	4.998

Mean 5.003

Table III. (cont.).

2. Moist air in open tube :—

No.	A.	B.	Mean.	$\lambda/2$.
8.	{ 35.0	35.3	35.102	5.023
	{ 35.15	35.2		
	{ 39.8	40.3		
9.	{ 40.1	40.1	40.075	5.009
	{ 45.2	45.3		
10.	{ 45.3	45.05	45.212	5.023
	{ 50.2	50.2		
	{ 50.2	50.1		
11.	{ 50.2	50.15	50.175	5.018
	{ 55.2	55.3		
12.	{ 55.2	55.1	55.20	5.018
	{ 60.2	60.3		
	{ 60.3	60.2		
13.	{ 65.2	65.2	65.175	5.017
	{ 65.2	65.1		
	{ 65.15	65.2		
Mean				5.018

TABLE IV.

Nitrous Oxide tube, 13°·5 C. :—

No.	A.	B.	Mean.	$\lambda/2$.
6.	{ 32.7	33.0	32.825	5.471
	{ 32.7	33.0		
	{ 32.7	32.9		
7.	{ 38.2	38.5	38.275	5.468
	{ 38.1	38.4		
	{ 38.2	38.25		
8.	{ 43.5	44.0	43.758	5.470
	{ 43.6	43.9		
	{ 43.7	43.85		
9.	{ 49.2	49.3	49.275	5.475
	{ 49.0	49.45		
	{ 49.2	49.5		
10.	{ 54.5	54.9	54.733	5.473
	{ 54.6	55.0		
	{ 54.7	54.7		
11.	{ 60.15	60.5	60.226	5.478
	{ 60.1	60.5		
	{ 60.1	60.25		
12.	{ 65.6	65.7	65.65	5.471
	{ 65.6	65.7		
13.	{ 71.15	71.25	71.175	5.475
	{ 70.9	71.2		
14.	76.55	76.6	76.575	5.470
15.	{ 81.8	82.0	82.00	5.467
	{ 81.9	82.1		
	{ 82.0	82.2		
16.	87.35	87.4	87.375	5.461
17.	{ 92.9	93.1	93.00	5.470
	{ 92.85	93.15		
Mean			5.471	

TABLE V.

Air Comparison tube at 13°·5 C. :—

No.	A.	B.	Mean.	λ/2.
	35·4	35·4		
5.	35·4	35·5	35·425	7·085
	42·5	42·4		
6.	42·4	42·5	42·450	7·075
	49·5	49·5		
7.	49·5	49·55	49·512	7·073
	56·6	56·6		
8.	56·55	56·6	56·588	7·073
	63·6	63·6		
9.	63·6	63·8	63·650	7·072
	70·6	70·7		
10.	70·65	70·7	70·663	7·066
	77·7	77·7		
11.	77·65	77·7	77·687	7·063
	84·7	84·7		
12.	84·8	84·85	84·862	7·072
Mean				7·072

This, when corrected for *dry* air at 13°·5 C., becomes :

$$\frac{7·072 \times 5·003}{5·018} = 7·052 \text{ cms.}$$

Nitric Oxide.

The method employed for nitric oxide was similar to that used for nitrous oxide, the only alteration being the substitution of the generating apparatus by a larger one. This was rendered necessary by the comparatively low solubility of the substances employed. Pure nitric oxide was prepared by dropping a solution of potassium ferrocyanide and potassium nitrite into dilute acetic acid. The lower vessel, containing the acetic acid, was provided with a small dropping funnel and an exit tube, closed by a tap, so that it could be emptied and recharged with acid without disconnecting any of the apparatus. The first drying-tube, which for nitrous oxide contained calcium chloride, was replaced by one containing broken stick potassium hydroxide. The mercury in the manometer was protected by a layer of strong sulphuric acid.

The only results previously obtained for nitric oxide

appear to be those of Regnault, Masson, and Heuse. Regnault* first prepared the gas by the action of nitric acid on copper, but afterwards substituted a method in which he reduced potassium nitrate by means of an acid solution of ferrous chloride. This method, as he states, gives almost pure nitric oxide. His results, at a mean temperature of $88^{\circ} \cdot 8$ C., lead to the values : $C_p = 7 \cdot 22$, $C_v = 5 \cdot 23$, $C_p/C_v = \kappa = 1 \cdot 380$. Masson †, using the method described under nitrous oxide, obtained a value $\kappa = 1 \cdot 414854$. The values $C_p = 7 \cdot 25$, $C_v = 5 \cdot 25$, $C_p/C_v = 1 \cdot 380$ were obtained by Heuse ‡. He prepared the gas by the action of nitric acid on copper, and purified it by absorption in ferrous sulphate solution and expulsion by subsequent warming.

The results obtained in the present series of experiments are tabulated below (Table VI.).

TABLE VI.

Tube 1.

No. of exp.	Dry air. λ .	NO. λ .	κ' .	ϕ .	κ .	Temp. ° C.
1.	13.342	13.050	1.389	—	—	6.0
2.	13.352	13.094	1.396	—	—	6.5
3.	13.398	13.104	1.390	—	—	8.0
4.	13.404	13.120	1.391	—	—	8.3
5.	13.390	13.118	1.393	—	—	8.3
6.	13.360	13.098	1.396	—	—	8.0
7.	13.432	13.138	1.390	—	—	8.4
Means ...	13.382	13.103	1.392	1.00184	1.394	7.6

Tube 2.

	$\lambda/2$.	$\lambda/2$.				
1.	8.356	8.567	—	—	—	6.8
2.	8.394	8.622	—	—	—	8.3
Means ...	8.375	8.594	1.379	1.00184	1.381	7.5

The discrepancy between tubes 1 and 2 is explained later.

* *Mém. de l'Académie*, vol. xxvi. p. 137 (1862).

† *Phil. Mag.* (4) xiii. p. 533 (1857).

‡ *Ann. Phys.* (4) lix. p. 86 (1919).

The Tube Correction.

It has been shown, both theoretically and experimentally, that the velocity of sound, u , in a gas contained in a relatively small tube, is somewhat smaller than that in the free gas. To obtain the true velocity, the corrections usually applied are: (i.) for the effect of the yielding of the walls of the tube*, and (ii.) for the effect of the diameter of the tube†. The first correction, in the case of gases, has an influence which is quite negligible unless the tube wall is very thin. When applied to the results given in Table II. it gives a value $u_{\text{true}}^2 = u_{\text{observed}}^2 \times 1.000095$ —a correction quite outside the limits of error of the experiment. A modified form of the second correction‡, when applied to the results in Table II., gives a result identical with that already given. The calculated value of Kirchhoff's correction does not agree with that found experimentally§. The experimental value is always greater, but by a very uncertain amount. The constant γ in Kirchhoff's formula is dependent on the viscosity and thermal conductivity of the gas contained in the tube. No account is taken of the thermal properties of the tube, or of the nature of its inner surface. Stürm|| has shown that these factors affect considerably the velocity of sound in a gas in a tube. The constant γ , if it is to be of any value, must include terms relating to the tube as well as to the gas. Hence the method of eliminating the tube constant by employing two or more tubes of different radii is not strictly accurate. It assumes a value of γ which is constant for all the tubes—a condition which is extremely difficult to realize experimentally.

The air tube used in the experiments described was a heavy thick-walled (4 mm.) tube, whilst gas tube 1 was much lighter. Gas tube 2 was a very light, thin tube. Unless the tube correction is eliminated between these tubes, measurements taken with them are not comparable. Since this comparison is the fundamental principle of this method of experiment, the elimination of the

* Lamb, 'Dynamical Theory of Sound,' 1910, p. 174.

† Kirchhoff, *Pogg. Ann.* cxxxiv. p. 177 (1868).

‡ Fürstenau, *Ann. Phys.* (4) xxvii. p. 735 (1908); Jeans, 'Dynamical Theory of Gases,' 2nd edit. p. 315.

§ Schneebeli, *Pogg. Ann.* cxxxvi. p. 296 (1869); Seebeck, *op. cit.* cxxxix. p. 104 (1870); Kayser, *Wied. Ann.* ii. p. 235 (1877); Müller, *Ann. Phys.* xi. p. 331 (1903).

|| *Ann. Phys.* xiv. p. 822 (1904).

effect of the tube used is very essential. The experimental results of Table VII. show this to be the case. To calculate the experimental value of the constant γ , the frequency must be known. The difficulty of determining accurately the frequency of the short shrill note emitted by the tube when rubbed, is apparent. It was therefore

TABLE VII.

Comparison of the gas tubes with the standard air tube.

Tube 1.

$\lambda/2$ air tube.	$\lambda/2$ gas tube.
6.869 cm.	6.798 cm.
6.871 "	6.836 "
6.871 "	6.869 "
6.862 "	6.867 "
6.861 "	6.861 "
6.872 "	6.849 "
6.861 "	6.860 "
6.865 "	
Means... 6.866 cm.	6.849 cm.

Ratio = $6.866/6.849 = 1.00248$ = the factor for tube 1.

Tube 2.

8.769 cm.	8.721 cm.
8.750 "	8.705 "
8.754 "	8.694 "
8.764 "	8.698 "
8.766 "	8.699 "
8.766 "	8.711 "
8.760 "	
8.764 "	
Means... 8.762 cm.	8.705 cm.

Ratio = $8.762/8.705 = 1.0065$ = the factor for tube 2.

decided to eliminate the tube correction instead of attempting to find its absolute value. To do this, all measurements were referred to the large air tube as a standard. The gas and air tubes were both filled with pure dry air, and the waves produced simultaneously in each were measured. The results are given in Table VII. The ratio $\lambda_{\text{air tube}}/\lambda_{\text{gas tube}}$, with dry air in each, was always greater than unity and a different ratio was found for the two

different gas tubes. If the wave-lengths obtained when the gas tubes were filled with nitrous or nitric oxides are now multiplied by the factor for the tube employed, the resulting wave-lengths will be strictly comparable with those for the air in the air tube. In the corrected results given in Tables VIII. and IX. it will be seen that the discrepancies between the two series of results in Tables II. and VI. disappear. This seems to be an important result, previously overlooked by experimenters. The advantage of this method over that of filling the air tube alternately with the gas and with air, is that a pure specimen of the gas under investigation is kept in a sealed tube. The difficulty of keeping the air tube, which is more or less open at one end, filled with a pure specimen of such a gas as nitric oxide is obvious. In addition, the waves are produced simultaneously in each tube, so that a difference of frequency is impossible.

TABLE VIII.

Calculation of results for Nitrous Oxide.

The mean wave-length of 5.483 cm. for nitrous oxide (Table II. tube 1) has now to be multiplied by the factor 6.866/6.849 (Table VII.). The true wave-length then becomes

$$\lambda/2 \text{ air} = 7.072 \text{ cm.}$$

$$\lambda/2 \text{ N}_2\text{O} = 5.495 \text{ ,,}$$

Using the physical constants $T_c = 308^{\circ}.5$ abs., $P_c = 75$ atmos., Mol. wt. = 44.02, for nitrous oxide, and the method of calculation given in the previous paper, the above wave-lengths lead to a value $\kappa = 1.302$ at $12^{\circ}.9$ C.

Similarly, the wave-length of 6.453 cm. (Table II. tube 2) is to be increased in the ratio 8.762/8.705, giving the final values

$$\lambda/2 \text{ air} = 8.356 \text{ cm.}$$

$$\lambda/2 \text{ N}_2\text{O} = 6.495 \text{ ,,}$$

giving a corresponding value of $\kappa = 1.302$ at $11^{\circ}.6$ C.

The final mean results are

$$\left. \begin{array}{l} \kappa = 1.302, \\ \text{whence } C_p = 8.799 \text{ gm. cal.} \\ C_v = 6.758 \text{ ,,} \end{array} \right\} \text{ at } 12^{\circ}.25 \text{ C.}$$

TABLE IX.

Calculation of results for Nitric Oxide.

As in the preceding table, the gas tube wave-lengths given in Table VI. require to be multiplied by the factor for their respective tubes. The final wave-lengths then become

$$\text{Tube 1. } \lambda \text{ air} = 13.382 \text{ cm.}$$

$$\lambda \text{ NO} = 13.130 \text{ ,,}$$

$$\text{Tube 2. } \lambda/2 \text{ air} = 8.594 \text{ cm.}$$

$$\lambda/2 \text{ NO} = 8.429 \text{ ,,}$$

The critical data used for nitric oxide are $T_c = 179^{\circ}.5$ abs., $P_c = 71.2$ atmos. The molecular weight is 30.

The first set of wave-lengths lead to a value $\kappa = 1.401$ at $7^{\circ}.6$ C., and the second to a value $\kappa = 1.399$ at $7^{\circ}.55$ C.

The final mean results are then given by

$$\left. \begin{array}{l} \kappa = 1.400, \\ C_p = 6.990 \text{ gm. cal.}, \\ C_v = 4.993 \text{ ,,} \end{array} \right\} \text{ at } 7^{\circ}.6 \text{ C.}$$

The results for nitrous oxide were also calculated, using Wohl's equation of state*. Values identical with those given above were obtained, and as the equation is more complicated than Berthelot's, it was not further employed.

Summary.

The ratios of the specific heats of nitrous oxide and of nitric oxide have been determined by a method depending on the relative velocities of sound in these gases and in air. The use of dry air, free from carbon dioxide, as a standard, has been shown to be necessary. It has also been proved that it is necessary to eliminate the effect of the tube on the velocity of sound in the gas contained in it. Wohl's equation of state has no advantage over that of Berthelot for the reduction of the results. Employing Berthelot's

* Nernst, 'Theoretical Chemistry,' 8th edit. p. 258.

430 Mr. P. Lasareff on *Number of Radiating Atoms of*
equation as the basis of calculation, the following results
were obtained :—

TABLE X.

	Nitrous Oxide. 12°·2 C.	Nitric Oxide. 7°·6 C.
Cp/Cv	1·302	1·400
Cp	8·799 gm. cals.	6·990 gm. cals.
Cv.....	6·758 „	4·993 „

In conclusion, the authors wish to express their thanks to the Kent Education Committee for a maintenance grant to one of them (W. G. S.), and to the authorities of East London College for a grant which contributed to defraying the expense of the work. The experiments described were submitted as part of a Thesis for the Degree of M.Sc. in the University of London by W. G. Shilling.

East London College,
University of London.

XLVI. *On the Question of the Number of Radiating Atoms of Various Dimension within Gaseous Hydrogen, studied from the point of view of Bohr's Atom Model.* By P. LASAREFF, Member of the Academy of Sciences of Petrograd, Director of the Physical Institute of Moscow*.

THE dimension of the hydrogen atom calculated from Rutherford-Bohr's theory is determined by the radius a of an electron moving round the centre as :

$$a = \frac{h^2}{4\pi^2 m e^2} \tau^2, \quad (1)$$

h is Planck's constant, m the electron mass, e its charge, and τ any whole number from 1 to ∞ , representing the order of the electron's stable orbit. In the case of a single atom, its dimensions are determined by the formula (1), τ is arbitrary. If we have many atoms, subject to mutual shocks, the dimensions of the electron's orbit, as is easy to understand, could not surpass a certain limit, because of the mutual influence of the electrical fields of atoms. In fact, it is experimentally proved that it is possible to observe only spectral lines for which τ varies from 1 to 15, and in that case the dimensions of the electron orbits are :

from $2a = 1·1 \cdot 10^{-8}$ cm. ($\tau=1$)
to $2a = 247·5 \cdot 10^{-8}$ cm. ($\tau=15$).

* Communicated by the Author.

Orbits surpassing the last one are impossible because of the reciprocal shocks of the atoms and the mutual influence of the fields. Rarefaction of the gas permits the maximum of the atom's dimension to increase, and, indeed, in star spectra, spectral lines of hydrogen have been found indicating the existence of atoms with an electron orbit of the order 33. It appears of interest to find out the relative number of atoms of gas radiating and possessing electron orbits of different orders.

As is known, Bohr shows that radiation takes place within hydrogen at the moment when one electron displaces itself from one stable orbit of order τ_0 , to another stable orbit of order τ_1 , while the light-energy radiated at the times of such a movement equals $q = h\nu$, where ν denotes the frequency of oscillation of the radiated line, and q is determined by the formula

$$q = \frac{2\pi^2 me^4}{h^2} \left\{ \frac{1}{\tau_1^2} - \frac{1}{\tau_0^2} \right\}.$$

If the gas contains N atoms, which emit in one time-unit, at the moment of the electron's displacing from orbit τ_0 to orbit τ_1 , a radiation with the wave-length λ (frequency of oscillation ν) then the light-energy radiated by the gas in a time-unit will equal

$$\epsilon = q \cdot N.$$

As $q = h\nu = \frac{hc}{\lambda}$ where c is light-velocity, we have

$$\epsilon = \frac{Nhc}{\lambda} \quad \text{or} \quad N = \frac{\epsilon\lambda}{hc}.$$

If we call $N_{\max.}$ and $(\epsilon\lambda)_{\max.}$ the maximum values of N and $\epsilon\lambda$, we have

$$\frac{N}{N_{\max.}} = \frac{\epsilon\lambda}{(\epsilon\lambda)_{\max.}}.$$

Thus, knowing the energy of definite spectral lines ϵ_1, ϵ_2 , and their corresponding wave-lengths λ_1, λ_2 , we are able to find out the relative number of N in parts of maximum value $N_{\max.}$, and consequently the distribution of radiating atoms. In the present work we have found out the relative quantities of atoms having electrons displacing themselves from the third, fourth, and fifth orbit to the second one, producing radiation of the first three lines of Balmer's series with wave-lengths equalling $656\mu\mu$, $486\mu\mu$, and $434\mu\mu$. For the purpose of finding the energy ϵ of a definite spectral line, the spectrum of hydrogen in Geisler's tube has been spectrophotometrically compared with the intensity of Hefner's lamp, for which the distribution of energy in the spectrum

has been studied by Ångström. Knowing the relative intensity of the line J_0 and the energy corresponding to the radiation of a wave of the same length in Hefner's lamp J_H , we get the relative value of $\epsilon = J_0 \cdot J_H$. Multiplying $J_0 J_H$ by the corresponding λ we find the relative value N , which, divided by $(J_0 J_H \lambda)_{\max}$, gives a relative value of N (the $N_{\max}$ being accepted as unit).

Heisler's hydrogen tube was excited by a large inductor with an Apex gas interrupter. This interrupted current was chosen of such an intensity that the brightness of the light on the field of König-Marten's spectrometer would be convenient for photometry.

The tube was placed in parallel to the one spectrometer's slit, and with the help of a lens was projected at that one slit; a prism of total reflexion was installed opposite the other slit, sending through that second slit rays of Hefner's lamp.

The results obtained may be found in the Table below, in which τ designates the order of the orbit from which the electron had displaced itself to the second orbit:

TABLE.

λ .	τ .	$\frac{N}{N_{\max.}}$
656	3	1.000
486	4	0.251
434	5	0.175

From all the measures quoted it will be seen that in Heisler's tube, radiating under the influence of an electric discharge and filled with hydrogen, most of the electrons causing the radiation move over from the third orbit to the second. The quantity of electrons springing from the fourth orbit to the second equals only 25 per cent. of that first quantity and, at last, the quantity of electrons springing over from the fifth to the second orbit equals only 17 per cent.

Thus the quantity of springing electrons decreases with the increasing of the distance of electrons from the centre.

It appears of interest to study further members of Balmer's series and also Lyman's series, that result from the displacing of electrons to the first orbit.

The first of those problems is pointed out as one to be experimentally studied at the Physical Institute.

In conclusion I express my gratitude to Ingenieur V. Lasarev for his photometric work and assistance in calculations.

Physical Institute,
Miusskaja Pl., Moscow.

XLVII. *Positive Rays in simple Gases.*

By J. J. McHENRY, M.Sc. N.U.I.*

THE object of the following experiments was to study the proportion of atomic and molecular positive rays of the simple gases, under varying conditions of pressure, etc., in the discharge tube. It has been pointed out by Sir J. J. Thomson that such a study would probably throw some light on the nature of ionization by cathode rays and the positive rays themselves, and also give some information on dissociation and the forces that bind the atoms in a molecule together.

The apparatus used was essentially the same as that described by Sir J. J. Thomson in 'Rays of Positive Electricity,' p. 57. The Kanalstrahlen were given a horizontal deflexion by means of an electrostatic field and then were deflected vertically on to a parabolic slit by means of a magnetic field. Behind the slit was a Faraday cylinder connected to a quadrant electrometer. The currents registered by the electrometer were proportional to the numbers of positive rays falling on the slit and are given throughout in arbitrary units.

The fast or slow positive rays could be analysed as desired by using a large or small electrostatic field to deflect them on to the slit. In our experiments a field of 40 volts between the plates gave us our slow Kanalstrahlen, while those of higher energy could be brought on to the slit by fields of 80-300 volts. In order to understand this method of working, it is convenient to remember the following facts. The energy possessed by a positive ray is proportional to the voltage E through which it has fallen to the cathode,

$$\text{or } Ee = \frac{1}{2}mv^2.$$

Its energy is also proportional to the field required to give it a fixed horizontal deflexion, thus in our experiments, if a voltage V between the plates is required to impart a horizontal deflexion equal to that of the slit, this voltage V is proportional to the energy of the positive ray. In the curves shown, then, and marked 40 volts, 80 volts, etc., the energy possessed by the Kanalstrahlen examined is proportional to the voltage figure shown. Also if a magnetic field H brings the Kanalstrahlen of a given mass on to the slit when the voltage between the plates is V , then from the relation $V^2/H = \text{const.}$ we can calculate the magnetic field that would be required with any other voltage.

Finally, when V is fixed if a magnetic field H brings the

* Communicated by Sir J. J. Thomson, O.M., F.R.S.

Kanalstrahlen of mass " m " on to the slit, from the relation $H^2/m = \text{constant}$ can be found the field required to bring those of any other mass on to the slit.

In performing the experiment V was kept constant, and a curve plotted showing the deflexion of the electrometer against H the magnetic field, as explained (*loc. cit.* pp. 58-59). The curves we obtained in this way were not very sharp, owing to a slight rotation of the slit, but were sufficiently so to enable us to separate clearly the molecular from the atomic Kanalstrahlen in the simple gases.

In our preliminary experiments with oxygen, the ratio O_1/O_2 was found to be very unsteady—sometimes the atom and sometimes the molecule predominated. It was then found that the presence or absence of mercury in the discharge-tube accounted for the phenomenon. The gas used was stored in a mercury reservoir and then flowed through a capillary tube into the discharge-tube, the pressure being kept low by means of a Gaede mercury pump. The gas was thus always more or less contaminated with mercury vapour.

To test the effect of mercury vapour on the ratio O_1/O_2 the gas was passed over a tube cooled in liquid air in order to remove the mercury vapour.

When the discharge had taken place for some time and the mercury removed by the liquid air-trap, O_1/O_2 was found to be about $\frac{1}{3}$ —the molecular positive rays being about three times as numerous as the atomic ones. When mercury was allowed into the tube, by removing the liquid air from the trap, the ratio O_1/O_2 became about 1. This was repeated several times and the molecule could always be brought into great prominence by removing the mercury by cooling.

The following table further illustrates this point. The first two columns give the number of atomic and molecular positive rays in oxygen from which the mercury had been removed by cooling in liquid air. The molecular positive rays are much the more numerous. In the second two columns the mercury was not removed, and here it will be seen that the atom predominates:—

TABLE I.—Oxygen.

	Without Mercury.		With Mercury.	
	O_1 .	O_2 .	O_1 .	O_2 .
$V=40$	245	190		
$V=80$	220	>800	off scale	400
$V=120$	135	575	>600	250
$V=160$	35	125	140	80

It will be noticed in the last two columns that the atomic positive rays were more numerous than the molecular, even in those of highest energy, as shown by the last numbers ($V=160$).

This is important, because in all of our experiments with pure oxygen, the fastest positive rays are mostly molecular, even at very high pressures. The same rule applied to positive rays in hydrogen and nitrogen.

This effect of mercury, of causing the Kanalstrahlen to be mostly atomic, seemed to take place only when oxygen was in the tube. The presence of mercury seemed to have no effect on nitrogen positive rays. In one experiment the nitrogen Kanalstrahlen were analysed when there was no mercury vapour in the tube, the positive column showing the familiar nitrogen pink colour. The experiment was repeated with so much mercury in the tube that the pink colour in the positive column entirely disappeared, and only the greyish colour of the mercury discharge was seen. The curves obtained in the two cases were practically identical, so that the presence of mercury vapour did not seem to affect the nitrogen Kanalstrahlen. Similarly, we found no effect of mercury on the hydrogen Kanalstrahlen. It may be that radiation emitted by the mercury in the tube can cause the dissociation of the oxygen molecules, while not affecting nitrogen or hydrogen. This point will be referred to later.

In order to eliminate mercury from the discharge-tube, we placed a cooling trap on either side of the discharge-tube. One trap prevented mercury or other vapours from entering the tube with the gas stream, while the other trap prevented the diffusion of mercury from the pump into the discharge-tube, the traps being kept in liquid air.

Production of Atomic Positive Rays near the Cathode.

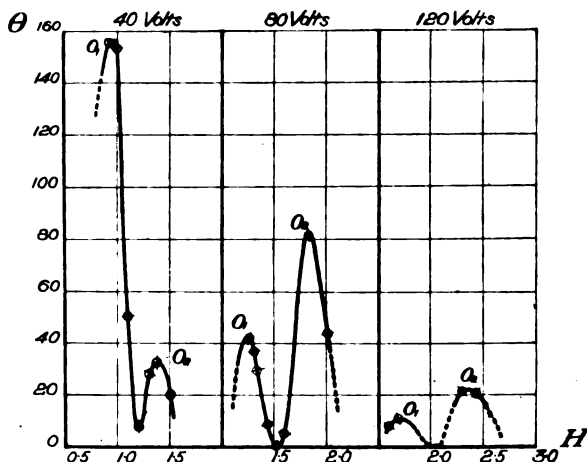
With the gas thus purified a series of experiments was made with oxygen, the Kanalstrahlen of different energies being brought on to the slit as described by different electrostatic fields between the plates. In all the experiments the slower Kanalstrahlen, brought on the slit by 40 volts between the plates, were mostly atomic, while those of greater energy were mostly molecular.

Since the energy of a positive ray depends upon the potential difference through which it falls into the cathode, those of small energy are those produced near the cathode, while those of greater energy are produced at greater distances from the cathode, if we assume that they suffer no loss of energy by collision, etc. The production of atomic

Kanalstrahlen near the cathode is very noticeable at high pressures, but, even at the very highest pressures used, the faster positive rays are mostly molecular. This will be seen in figs. 1, 2, and 3.

In fig. 1 the pressure of the oxygen in the discharge-tube was such that, with a potential of about 5000 volts on the tube (equivalent spark-gap 1 mm.), a current of 2 milliamperes passed through, and the boundary of the dark space was clearly visible, the length of the dark space being about 4 cms. In the 40 volts curve the atomic peak is very striking. The molecule is more numerous in the 80 and

Fig. 1.



120 volt curves than the atom. Fig. 2 is taken with a slightly lower pressure, the current through the tube being about 1 milliampere, and the potential on the tube about 6000 volts. The atomic peak in the 40 volt curve is now depressed and the molecular peaks in the 80 and 120 volt curves are raised. Fig. 3 is taken at lower pressure still, the voltage being about 11,000 and the current little more than .6 milliamp. The atom is of the same order as the molecule in the 40 volt curve, but in the succeeding curves, 80, 120, and 160 volts (the latter not shown in the figure), the molecular positive rays are about three times as numerous as the atomic.

These general features are reproduced in the analysis of hydrogen and nitrogen positive rays. Curves very similar.

to fig. 1 are obtained with hydrogen when the tube is running a good deal harder than with oxygen, the equivalent spark-gap being 4 mm. (14,000 volts) and the current

Fig. 2.

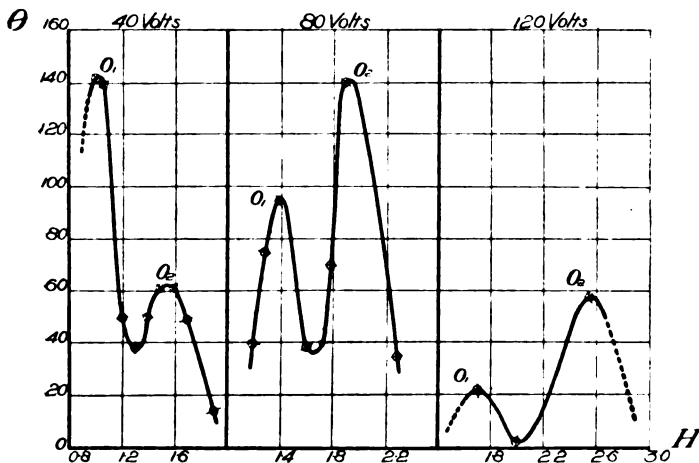
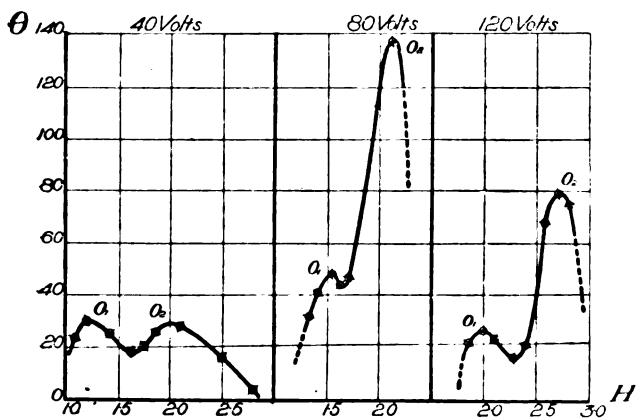


Fig. 3.



through the tube .3 milliamp. Running the tube harder still the curves become like those shown in fig. 3 for oxygen.

A simple explanation of these results is obtained if we suppose the molecular positive rays to be produced by

cathode rays, while the positive rays themselves when they ionize the gas tend to produce atomic rather than molecular ions. When a primary cathode ray collides with a molecule and ionizes it, the electron knocked off soon acquires sufficient speed under the fall of potential in the dark space to be again able to ionize. Ionization by the cathode rays or electrons increases, then, as we go away from the cathode, so that most of the Kanalstrahlen thus produced fall through the greater part of the potential fall of the dark space, and consequently constitute the faster positive rays. These we have found in our experiments to be mostly molecules.

Ionization by the positive rays, on the other hand, would increase towards the cathode, though it is appreciable all through the dark space, as a positive ray needs to fall through a field of only about 100 volts in order to ionize. The ions produced by the positive rays themselves are then mostly formed near the cathode, and these slow positive rays we found to be mostly atomic.

On this view, then, ionization by cathode rays in general takes place without the dissociation of the molecules, while the more violent nature of the ionization by the positive rays produces charged atoms, one or both of which are positively charged.

The explanation of the results may, however, not be quite so simple. It is pointed out by Dr. Aston (Proc. Camb. Phil. Soc., May 1920) that the energy distribution of the positive rays in hydrogen greatly depends upon the shape of the cathode. When the cathode was convex, so that the cathode rays were not concentrated along the axis of the tube, the results obtained by Dr. Aston were similar to ours—the fast Kanalstrahlen were molecular, the slow ones atomic, the energy of the molecular positive rays being about twice that of the atomic, so that their velocities were the same. These slow atoms are attributed by Dr. Aston to the dissociation behind the cathode of molecular positive rays into two atoms, one positively charged, the other neutral. The primary molecular rays he supposes to be those ions which drift from the negative glow into the dark space, and fall into the cathode under the fall of potential in the dark space.

With concave cathodes, Dr. Aston found that the atomic positive rays were the primary ones, and molecules were formed by the capture of a neutral hydrogen atom. In this case the fast Kanalstrahlen were atomic—the slower ones molecular. As the use of a concave cathode produces a large increase in the intensity of the axial cathode beam, he

attributed the formation of the atomic Kanalstrahlen to the cathode rays.

Further experiments by the electrical method would be required to study these points, using cathodes of different shapes. The cathode used in our experiments combined the convex and concave shapes, being concave close to the centre, and gave a well-pronounced axial beam of cathode rays. It was not altered during the course of the experiments. However the atomic and molecular positive rays are produced, the similar behaviour of oxygen, nitrogen, and hydrogen positive rays found by us shows that the mechanism of ionization and dissociation in discharge-tubes is the same for all three simple gases.

Deflexion of Cathode Rays by Magnet.

In our experiments the cathode was so shaped that it gave rise to a conical beam of cathode rays which struck the glass well of the discharge-tube in a broad circular green patch of about 2 cms. radius. The beam was concentrated at the axis of the cone, showing up as a clear line traversing the dark space when the pressure was high. It is evident that only those positive ions which are produced along the axis of the cathode become positive rays. If a positive ion is produced at a distance from the axis of the tube it falls into the cathode obliquely, and hence does not become a positive ray as it does not pass through the cathode capillary tube.

Now, if a horse-shoe magnet is placed with one pole above and one pole below the cathode, the cathode rays are deflected from the axis. The further we go from the cathode the more the cathode rays are displaced from the axis, while close to the cathode the rays are only slightly deflected. The slow Kanalstrahlen produced by the cathode rays should be only slightly affected, while the faster ones produced further out should be greatly diminished, when the cathode rays are deflected by the magnet.

This experiment was tried with oxygen at moderate pressures. The cathode rays were given such a deflexion that the circular patch of green phosphorescence opposite the cathode moved a distance equal to its own diameter (4 cms.). Readings were taken of the atomic and molecular positive rays when the cathode rays were deflected, and also when they were undisturbed. The results are shown in the following table, the last column giving approximately the

percentage reduction caused by the deflexion of the cathode beam :—

TABLE II.

	Cathode rays not deflected.	Cathode rays deflected.	Per cent. reduction.
40 volts.			
Oxygen atom, O_1 ...	205	105	48
" mol., O_2 ...	95	60	36
80 volts, O_1	67	35	53
" O_2 ..	175	63	65
120 volts, O_1	23	10	56
" O_2	120	14	92

The table shows that the slowest molecular positive rays are reduced by 36 per cent., those of medium energy by 65 per cent., and the fastest ones by 92 per cent. when the cathode rays are deflected. The molecular positive rays are thus reduced in increasing measure as we go away from the cathode. This is not so marked in the case of the atomic positive rays. It would then seem likely that the molecular Kanalstrahlen are produced by the beam of primary cathode rays. The large reduction in the number of slow atoms is probably due to the reduction of the faster molecules.

With hydrogen in the tube similar results were obtained, as shown in the following table :—

TABLE III.

	Cathode rays not deflected.	Cathode rays deflected.	Per cent. reduction.
80 volts, H_1 ...	215	86	60
" H_2 ...	110	80	27
160 volts, H_1 ...	71	35	51
" H_2 ...	95	43	55

The reduction in hydrogen numbers is of the same order as that in oxygen, it cannot therefore be due to any loss by deflexion of the Kanalstrahlen themselves.

Mixtures of Hydrogen and Oxygen.

Some experiments were now performed with mixtures of various proportions of hydrogen and oxygen in the discharge-tube, with a view to finding if the energy distribution of the hydrogen atom and molecule was the same as that of the oxygen atom and molecule. The gases were mixed in the required proportions and allowed to flow into the discharge-tube through a long capillary tube. A remarkable feature of these experiments is that the hydrogen Kanalstrahlen were always few in comparison with the oxygens and not in proportion to the volume of hydrogen in the discharge-tube. This does not agree with Sir J. J. Thomson's results (*Phil. Mag.*, Aug. 1912, p. 247). There may have been more absorption in our experiments, as we worked with higher pressures, though we might expect, owing to the smaller area which the hydrogen molecule presents for collision to a cathode ray or positive ray, that the number of hydrogen ions produced should be smaller than the number of oxygen ions.

The following table shows the number of hydrogen and oxygen Kanalstrahlen in an experiment with two volumes of oxygen and one volume of hydrogen :—

TABLE IV.

	O ₁ .	O ₂ .	H ₁ .	H ₂ .
80 volts	456	500	50	54
120 „	230	380	20	45
160 „	23	55	small	small

It will be seen that the hydrogen and oxygen Kanalstrahlen behave similarly, and that the ratio O₁/O₂ is practically the same as that of H₁/H₂, so that the energy distribution of the hydrogens is similar to that of the oxygens.

The experiment was then performed with two volumes of hydrogen to one volume of oxygen, and in this case it will be seen that, while the hydrogen molecular positive rays were more numerous than the atomic ones, the reverse was the case for oxygen, as the following table shows :—

TABLE V.

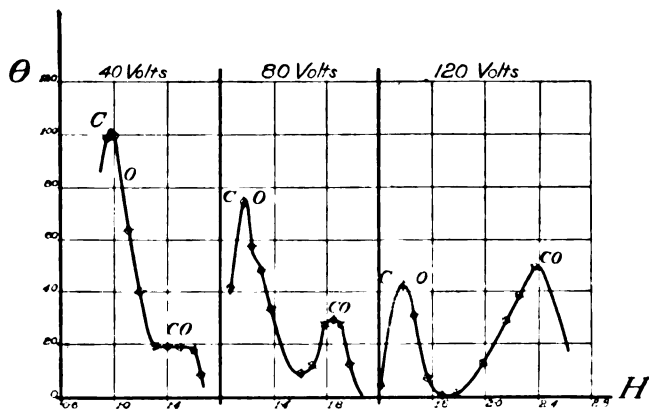
	O ₁ .	O ₂ .	H ₁ .	H ₂ .
40 volts	200	140	small	(H ₁ > H ₂)
80 „	308	184	90	112
120 „	216	220	24	84

The same points will be found in the experiment quoted by Sir J. J. Thomson (Phil. Mag. p. 247 (1912)). In the curves he shows that when the proportion of oxygen was high the molecule predominated, when low the atom came into prominence. Under the conditions of these experiments, however, if $(OH) +$ were formed in large quantities, it would come on the slit for about the same value of magnetic field as the oxygen atom.

Carbon monoxide.

A few experiments were performed with carbon monoxide in the discharge-tube. The proportion of atomic Kanalstrahlen is much greater than with pure oxygen under similar conditions. This will be seen from fig. 4, which

Fig. 4.



shows an analysis of CO. In this experiment the tube was quite hard and the pressure low. The equivalent spark-gap was about 6 mm., showing a potential of about 17,000 volts on the tube. Under similar conditions with oxygen the atomic peaks would be very small, as shown in fig. 3.

An analysis of CO by the electrical method is given by Dr. Aston (Phil. Mag. p. 246 (1912)), and here the molecular peak CO is very high in comparison with the atomic numbers. A field of 320 volts, however, was used by Dr. Aston to bring the particles on the slit, so that his tube was probably harder than ours and the pressure lower.

The ease with which this carbon compound is broken up suggests a possible explanation for the effect which we attributed to mercury of making the oxygen Kanalstrahlen mostly atomic. If the oxygen passing into the tube and coming in contact with tap-grease, etc., brought with it an appreciable quantity of hydrocarbons, or formed CO_2 and CO, these impurities (except CO perhaps) would be removed

with the mercury vapour when passed over liquid air, and would pass into the tube again when the liquid air was removed. The gases CO_2 and CO cause a coloration in the discharge-tube similar to that of mercury, while the presence of mercury is most easily detected spectroscopically.

We tried one experiment where this source of error was eliminated. The usual liquid air-traps were on either side of the discharge-tube, so that the oxygen was free from all vaporous impurities. A side-tube was connected directly to the bulb containing a small pellet of mercury, and this was warmed to make the mercury pass into the discharge-tube. When this was done, however, the tube became rapidly so hard that it was impossible to take any observations, the discharge becoming irregular and finally ceasing. The mercury vapour, perhaps, in being absorbed by the two cooling tubes swept the gas out along with it. This point was not further investigated, as the ease with which CO was broken into atoms had not then been observed.

If this supposition that carbon compounds and not mercury vapour are responsible for the effect we observed in oxygen be correct, it would explain why similar effects were not obtained with nitrogen and hydrogen, as these most inactive gases would not attack the stopper-grease and cause the carbon compounds to come into the tube.

A series of experiments with concave and plane cathodes, using the electrical method to measure the Kanalstrahlen, would give interesting results bearing on the suggestions made in this paper.

The energy distribution of the positive rays is best studied by using quite a short parabolic slit—that used in our later experiments being only about 4 mm. long. The use of this short slit enables the energy distribution to be ascertained sharply, as it prevents overlapping of slow and fast Kanalstrahlen in the measurements. Figs. 1 and 4 were obtained with the short slit. The positive ray current was still big enough to be easily measured by our electrometer, which in our experiments was never used at its highest sensitivity. It would be a great advantage to have the slit cut in a plate separate from the rest of the apparatus, and waxed on, so as to admit of easy alteration both in position and size. Also, instead of an induction-coil with its intermittent discharge, a steady source of high potential would be a great advantage in these experiments.

The above experiments were carried out in the Cavendish Laboratory, Cambridge, at the suggestion of Sir J. J. Thomson, O.M., for whose kind interest and direction throughout the work the author is extremely grateful.

XLVIII. Ionization by Collision. By J. S. TOWNSEND,
F.R.S., Wykeham Professor of Physics, Oxford.*

1. **S**EVERAL suggestions have recently been made with regard to the processes of ionization occurring in discharges through gases, but in many cases they do not appear to have been carefully considered in relation to the principal properties of the phenomena to which they are applied. There are various hypotheses on which some properties of electric currents might be explained; but in order to obtain a satisfactory theory, it is necessary to account for various types of discharge and for the small currents obtained with forces less than those required to produce a disruptive or a glow discharge. In most of the explanations that have been proposed, the ionization has been attributed either to direct or indirect effects of collisions of electrons and positive ions with molecules of the gas or to electrons set free by collisions of positive ions with the negative electrode.

2. In order to test the theory of ionization by collision which I gave many years ago, several sets of experiments had been made on the currents obtained between parallel plates when the initial conductivity was produced either by Röntgen rays or by ultra-violet light. The rate of increase of the current with the distance between the plates was measured for definite electric forces and pressures of the gas, and it was found that the development of the currents was independent of the initial ionization. Thus when ultra-violet light traversed the gas and fell on the negative electrode, the proportion in which the current increased with the distance between the plates was the same with strong light as with light of small intensity. It is therefore clear that the radiation which set free the electrons from the negative electrode did not affect the gas in such a way as to facilitate the genesis of ions by collision. The currents in all these cases were very small, and the number of collisions between electrons or ions with molecules of the gas in the course of an experiment was small compared with the number of molecules in the path of the current. The ratio of the number of collisions to the number of molecules was generally much less than $1:10^4$; so that in these experiments two collisions with the same molecule occurred very rarely, and effects that may arise

* Communicated by the Author.

from this cause would be inappreciable. If, for example, a molecule is dissociated by one collision, the number of atoms would be very small compared with the number of molecules in the gas, and the number of electrons generated by collisions with atoms is negligible in comparison with the number generated by collisions with molecules. This is also proved by the fact that the proportion in which the current increases with the distance between the plates is independent of the number of electrons set free initially from the negative electrode. In forming a theory to account for the increase of current with the electric force or with the distance between the plates which is observed in these experiments, it is unnecessary to consider ions which might be formed as a result of two collisions with the same molecule, or by collisions of electrons with molecules that may have been disturbed from their normal state by radiation.

The experiments show that the increase of the currents with the distance between the plates is due principally to ionization of molecules of the gas by the collisions of the electrons, since the number n of electrons arriving at the positive electrode is given by the formula $n = n_0 e^{ax}$ for a considerable range of distances x between the plates, when the electric force X is constant. With larger distances between the plates the currents increase more rapidly than the value of n as given by this formula, and eventually at a certain distance S a spark discharge is obtained with the potential $S \times X$. Thus it is necessary to assume that another process of ionization is taking place, in addition to the direct effect of the electrons, which does not produce any remarkable effect in the currents obtained with the shorter distances x , but has a large effect as x approaches the sparking distance S .

The additional ionization may apparently be attributed to ionization of molecules of the gas by the collisions of positive ions, or to electrons set free from the negative electrode by impacts of positive ions, or to radiation from molecules of the gas falling on the negative electrode and setting free electrons, this radiation being due to collisions of electrons with the molecules. The question then arose as to which of these modes of producing ions combined with the direct ionization by the collisions of electrons with molecules gives the most satisfactory explanation of the sparking-potentials when the pressure of the gas is above that corresponding to the minimum sparking-potential, and of the small currents obtained with

various distances between the electrodes when ultra-violet light from an external source falls on the negative electrode.

There were several reasons for attributing the additional ionization to the collisions of positive ions with molecules of the gas, and this theory is supported by the results of many recent experiments.

3. Some of the experiments bearing on these points have been made only with simple gases such as nitrogen and hydrogen, but the general conclusions to which they lead probably apply also to monatomic gases. Also, in the experiments on the conductivity between parallel plates and the corona discharges from the surface of a wire to a coaxial cylinder the electrodes have been made of ordinary metals such as copper, zinc, silver, etc., and it is impossible to apply the general conclusions deduced from these experiments to cases where the electrodes are of magnesium or alkali metals. With these metals, large numbers of electrons are set free from the surface by the action of ordinary light, and electric discharges between electrodes of these metals are maintained with comparatively small forces. This is probably due to the action of radiation from the discharge or to the impact of positive ions which cause large numbers of electrons to be set free from the surface of the alkali cathode under conditions where very few electrons would be set free from a cathode of an ordinary metal*.

4. The currents obtained between parallel plates at various distances apart when ultra-violet light falls on the negative electrode may be compared with formulæ for the currents obtained on the hypotheses which have been suggested above. The formulæ† have already been given for the case (A) where α is the average number of molecules of the gas ionized by an electron in moving through a centimetre in the direction of the electric force, and β the number of molecules ionized by positive ions, and the case (B) where a similar action is attributed to the electrons, but the positive ions, instead of ionizing molecules of the gas, are supposed to contribute to the ionization by setting free electrons when they collide with the negative electrode.

The formulæ for the number n of electrons reaching the

* 'Electricity in Gases,' pp. 409, 437.

† 'Electricity in Gases,' pp. 315, 331.

positive electrode under these two conditions are :

$$(A) \quad n = n_0 \frac{(\alpha - \beta) \epsilon^{(\alpha - \beta)x}}{\alpha - \beta \epsilon^{(\alpha - \beta)x}},$$

and

$$(B) \quad n = n_0 \frac{\epsilon^{\alpha x}}{1 - \gamma(\epsilon^{\alpha x} - 1)}.$$

In the second formula the coefficient γ is the ratio of the number of electrons set free by impacts from the cathode to the number of positive ions that impinge on the surface.

In order to obtain a formula for the third case (C), where, in addition to the ionization produced by the collisions of electrons with molecules of the gas, some electrons are supposed to be set free from the cathode by the radiation from molecules of the gas, it is necessary to consider the question of the absorption of the radiation by the gas.

Definite information on this point, and on other points connected with the hypotheses which may be adopted to explain the currents between parallel plates, is obtained from experiments on the currents between a wire and a coaxial cylinder. The force at the surface of a wire required to maintain a glow discharge is connected by a definite relation with the sparking-potentials for parallel-plate electrodes, which shows that the currents obtained in the two cases depend on the same processes of ionization, so that it must be possible to explain both types of discharge by the same hypothesis *. In the case of the radial field of force between a wire and a coaxial cylinder, there is a critical value X_1 of the force at the surface of the wire with which a small continuous glow discharge is maintained between the wire and the cylinder ; and if a be the radius of the wire, and b the radius of the cylinder, the force X_1 is independent of the radius b provided b is greater than a certain radius c . The value of c depends on a and on the pressure of the gas.

In order to account for the fact that X_1 is independent of b , it is necessary to assume in the case of a positive current flowing from the wire to the cylinder either that there are no electrons set free from the surface of the cylinder or that the same number are set free from a cylinder of large diameter as from a cylinder of small diameter. The force at the surface of the cylinder is aX_1/b , and by increasing the radius b the intensity of the electric force near the surface of the cylinder may be reduced so that electrons and positive ions would move with such small velocities in passing through

* *Electricity in Gases,* p. 369.

the space near the surface of the cylinder that they would not generate ions or excite radiation by colliding with molecules of the gas.

It is impossible, therefore, to obtain a satisfactory explanation of the positive currents from a wire to a coaxial cylinder, or the currents between parallel plate electrodes, on the assumption (B) that electrons set free from the negative electrode by impacts of positive ions form an important contribution to the processes by which the ionization is produced, as it is extremely improbable that the number of electrons thus set free is independent of the velocity with which the positive ions impinge on the electrode.

With regard to the third hypothesis (C), where electrons set free from the negative electrode by radiation from the gas are supposed to constitute an important effect, it would be necessary in this case to assume that the radiation emanating from the gas near the wire where the electrons and positive ions move with high velocities is not absorbed by the gas, as the number of electrons set free from the negative electrode must be the same when the radiation traverses different distances through the gas to cylinders of various diameters.

If it be assumed that the radiation is of this character, a formula for the currents between parallel plates is easily obtained, since nearly all the radiation from the gas falls on the electrodes when the currents traverse a small space near the centre of the field, and the distance between the electrodes is small compared with the diameter of the electrodes. If $\nu x \delta$ be the number of electrons set free from the negative electrode due to radiation excited by the collisions of a number ν of electrons in travelling through a distance x in the direction of the electric force, the formula (C) for the number n of electrons arriving at the positive electrode, when ultra-violet light from an external source acts on the negative electrode, is

$$(C) \quad n = \frac{n_0 \alpha e^{\alpha x}}{\alpha - \delta(e^{\alpha x} - 1)}.$$

When suitable values of the quantities α , β , γ , and δ are chosen, the values of n given by the three formulæ (A), (B), and (C) are found to be in good agreement with the small currents obtained between parallel plates at various distances apart when electrons are set free from the negative electrode by ultra-violet light from an external source. Also the sparking distance is found accurately by equating to zero the

denominators of the expressions multiplying the constant n_0 . In each case the same value of α is obtained, so that the experiments are decisive in showing that the ionization is principally due to the direct effect of collisions of electrons with molecules of the gas; but it would be impossible to decide from a set of these experiments which of the other modes of generating ions contributes the additional effect required in order to explain the disruptive discharge. When other experiments are considered, it becomes evident that the first hypothesis (A) is the only one of the three which is consistent with the properties of the currents obtained under various conditions.

5. The experiments on the conductivity of a gas between coaxial cylinders show that in the positive discharge from a wire to a coaxial cylinder it is very improbable that electrons set free from the cylinder by the impacts of positive ions contribute appreciably to the ionization, and if this were the determining factor it would be necessary to suppose that the number set free is independent of the velocity with which the positive ions collide with the negative electrode. This point may be tested by considering the values of γ obtained by comparing formula (B) with the currents between parallel plates for a given pressure of the gas when two different forces are used. For air at one millimetre pressure the values of α and γ are 5.25 and .00268 respectively when the force is 350 volts per centimetre and 6.3 and .0053 when the force is 437 volts per centimetre. Hence, in order to be in agreement with these experiments, the number of electrons set free from the negative electrode by impacts of positive ions should be doubled when the velocity of the positive ions is increased by increasing the electric force in the proportion 5:4. It must therefore be concluded that the second hypothesis cannot afford a satisfactory explanation of these phenomena.

In order to test the third hypothesis, it is necessary to consider the properties of metal surfaces in connexion with the emission of electrons due to incident radiation. The number of electrons emitted by the action of Röntgen rays or by ultra-violet light varies with different metals, and also with the state of the surface. In the case of ultra-violet light, the number of electrons emitted from a bright metal surface may be fifty times as great as the number emitted from the same surface after it has become oxidized. Hence, in the experiments on the development of currents between parallel plates, the factor by which the currents increase with the distance between the plates should vary with the state of the surface if the total ionization depends on the number of

electrons set free from the negative electrode by radiation from molecules of the gas. No such effect was observed in the earlier experiments, where the electrodes were of zinc, and the values of α and δ obtained by comparing those experiments with formula (C) are nearly exactly the same as the values obtained from the experiments with silver electrodes recently made by Ayres*.

Also, the currents between parallel plates of different metals have been measured by Gill† to test whether the factor by which the currents increase with the electric force depends on the sensitiveness of the plates to radiation. It was found that under the action of ultra-violet of constant intensity the number of electrons emitted from one plate was twenty times the number emitted from another, but the factor by which the currents increased with the electric force was the same with both plates. The experiments cannot therefore be explained on the hypothesis that electrons set free from the negative electrode by radiation from molecules of the gas make an appreciable contribution to the conductivity.

Thus the theory in which the principal effects are attributed to ionization of molecules of the gas by impacts of electrons and positive ions is the only one which affords a consistent explanation of the principal properties of the disruptive discharge between parallel plates, the glow discharge from a cylindrical surface, and the development of the smaller currents between parallel plates.

6. An objection to this theory is put forward in an account given in 'Nature' (vol. cx. p. 623, 4th Nov. 1922) of a theory of sparking-potentials communicated to the Academy of Sciences, Paris, by G. Holst and E. Oosterhuis, where it is stated that Holst and Oosterhuis have proved experimentally that the nature of the cathode has an important influence, and that they support the hypothesis that the positive ions do not produce ionization by contact with gas molecules, but by their electrostatic attraction they can liberate them from the cathode. It appears, however, from the account given in the *Comptes Rendus* (vol. clxxv. p. 577, 9th Oct. 1922), that in the experiments made by Holst and Oosterhuis the cathodes were of magnesium or alkali metals, and that their theory is only applied to monatomic gases at pressures near that corresponding to the minimum sparking-potential. It is quite clear that these experiments do not lead to general conclusions with regard to the properties of positive ions.

* T. L. R. Ayres, *Phil. Mag.* vol. xlv. p. 353 (Feb. 1923).

† E. W. B. Gill, *Phil. Mag.* vol. xlii. p. 852 (Nov. 1921).

It has been shown by Mey * that the cathode fall of potential in nitrogen, hydrogen, and helium is much less with cathodes of magnesium or alkali metals than with ordinary metals. It is probable that a similar difference due to the electrodes would be found in the minimum sparking-potentials for nitrogen and hydrogen as well as for the monatomic gases, but such a result would not prove that positive ions do not generate ions by collisions with molecules of the gas, or that electrons set free from the cathode by the impact of positive ions make an appreciable contribution to the ionization required to produce a disruptive discharge or a glow discharge from the surface of a wire when the electrodes are of ordinary metals.

7. In the theory of discharges given by Holst and Oosterhuis, the number of molecules ionized by electrons in moving from the negative to the positive electrode is calculated by a method based on unreliable assumptions relating to the conditions under which ions are generated by collisions. When an electron starting from rest moves through the gas under the electric force X , it is assumed that it makes several collisions with molecules in which there is very little loss of energy, and after traversing a certain distance a , it acquires a velocity corresponding to the ionizing potential V_1 , and ionizes a molecule of the gas. Thus two electrons start from rest from a plane at a distance a from the cathode, and four at a distance $2a$, the number arriving at the cathode being $2^{(S/a)}$, where S is the distance between the electrodes. The ionizing potential V_1 used in this calculation is the minimum potential under which a stream of electrons acquire sufficient kinetic energy to ionize an appreciable number of molecules of the gas, and it is assumed that the electrons moving through the gas never acquire a velocity greater than that corresponding to the potential V_1 . This would only be true if it were probable that a molecule would be ionized in most of the collisions where the velocity of the electron corresponds to V_1 . But there is no evidence to show that this is the case as the experiments by which the ionizing potential V_1 is found only indicate that ions are produced in appreciable numbers, which may be very small compared with the total number of collisions with molecules of the gas, when the electrons are moving with the velocity corresponding to V_1 . Also electrons lose energy in collisions which cause vibrations in molecules of the gas, as shown by ordinary Geissler tubes, and the experiments that have been

* K. Mey, *Ann. d. Phys.* (4) xi. p. 127 (1903).

made to determine the minimum ionizing potential V_1 indicate that the radiation from the molecules is appreciable when a stream of electrons collide with molecules with a velocity corresponding to a potential V_2 which is less than V_1 . If it were assumed that electrons lost all their energy in a large proportion of the collisions with the velocity corresponding to V_2 , they would very seldom attain a velocity corresponding to V_1 , if they made a large number of collisions with molecules of the gas in moving through the distance a under an electric force X .

In order to obtain ionization by collision it is necessary that the electrons should attain velocities greater than that corresponding to V_2 , and there is no reason to suppose that they do not also attain velocities greater than that corresponding to V_1 . Thus the method by which Holst and Oosterhuis calculate the number of molecules ionized by electrons moving through a given distance is not very reliable. The best test of the hypothesis, however, is to calculate by this method the total ionization produced by electrons moving through argon in a few particular cases and to compare the results with numbers found experimentally. When a small stream of electrons moves under a uniform force X , this theory implies that all the electrons attain a velocity corresponding to the ionizing potential V_1 at a series of distances from the cathode a , $2a$, $3a$, &c., where they lose all their energy by colliding with molecules, and this phenomenon recurs with perfect regularity for a large number of intervals, each of the same length a . If an electron starts from rest and moves under a constant force X , it loses a small proportion of its energy in the collisions with molecules before attaining the velocity corresponding to V_1 , so that the distance a is somewhat greater than V_1/X by an amount depending on the pressure of the gas. With the forces and pressures used in the following examples the distance a is very nearly equal to V_1/X , and it is only necessary to find the difference $(V_1/X - a)$ approximately. Various values have been found for the ionizing potential V_1 in argon from 12 to 15.1 volts, and in this calculation the largest value is taken, as it leads to numbers which come nearest to the results obtained experimentally.

8. If the argon be at 5.2 millimetres pressure and the force 208 volts per centimetre, the distance a is approximately $15.1/208 = .0725$ centimetre. From the numbers given by the author and Mr. Bailey* in the tables of mean

* J. S. Townsend and V. A. Bailey, *Phil. Mag.* vol. liv. p. 1033, Nov. 1922).

free paths and velocities of electrons in argon it will be found that in passing through this distance in the direction of the electric force, an electron makes on an average about 1300 collisions, in each of which it loses a proportion of its energy equivalent to about one part in 40,000.

The total loss of energy in traversing the distance a is therefore about 3 per cent. of the final energy, so that in order to attain the velocity corresponding to 15.1 volts the electron must traverse a distance .075 centimetre in the direction of the electric force. In order to make allowance for possible errors it may be supposed that the distance a is .08 centimetre. Hence the current would be increased by the factor $2^8=256$, if the distance between the plates were increased by .65 centimetre.

The currents obtained in argon between parallel plates of silver when ultra-violet light acts on the negative electrode have recently been determined by Ayres*, the gas having been purified very carefully. With the gas at 5.2 millimetres pressure, and a force of 208 volts per centimetre, it was found that the increase of current due to collision of electrons with molecules is given by the formula $n=n_0\epsilon^{\alpha x}$, where $\alpha=5.05$. Thus the current increases by the factor $\epsilon^{3.28}=26.5$, when the distance between the plates is increased by .65 centimetre.

The number obtained by the theory is therefore much too large, and instead of ionization taking place regularly at distances of .075 or .08 centimetre, it appears that on an average ionization occurs after the electron travels a distance of .137 centimetre, ($.137 \times 5.05 = \log_e 2$).

9. The preceding experiment where the gas was at 5.2 millimetres pressure is taken as an example, in order that there should be a large number of collisions with molecules when the electrons attain the velocity corresponding to V_1 , but when the ratio X/p is of the order 40, small quantities of impurities have a large effect on the value of α , and it might be suggested that the discrepancy between the theory and the experiments is due to this cause. With the larger values of the ratio X/p the effect of impurities is very much less, and it is comparatively easy to avoid errors due to impurities, so that the following experiment may be considered.

In argon at 1.325 millimetre pressure the value of α was found to be 5.76 when the electric force is 252 volts per centimetre, so that the current increases by the factor $\epsilon^{2.38}=17.8$ when the distance between the plates is increased

* T. L. R. Ayres, *loc. cit.*

by half a centimetre. In this case the distance a is approximately $\cdot 06$ centimetre, and an increase of half a centimetre in the distance between the plates would, according to the theory, increase the current by the factor $2^8 = 256$, which differs from the number obtained experimentally to a greater extent than in the example where the gas was at $5\cdot 2$ millimetres pressure.

If the values of α which have been obtained for helium be considered it will be found that the value of the ionizing potential usually given is too high. Experiments are being made on this point which will be described in a future communication.

10. There are many simple experiments which show that all the electrons do not acquire maximum and minimum velocities at the same regular intervals from the cathode, when a small current flows through a gas under a uniform electric force. Thus the experiments on the determination of the quality α , and the experiments on the motion of electrons in gases, show that the velocity of agitation and the velocity in the direction of the electric force becomes independent of the distance from the cathode after the stream has traversed a short distance through the gas, under a uniform electric force.

A distribution of the velocities where various effects due to impacts recur at regular intervals, occurs in the case of the striated positive column in a discharge-tube, but this phenomenon is only observed when the current is comparatively large and the electric force attains a maximum and minimum value in each striation, due to the charge in the gas.

11. The question arises as to what extent the mean loss of energy of electrons in collisions with molecules is affected when the velocity of the electrons is increased from below the critical value corresponding to the potential V_1 to a velocity above this value.

Several experiments have been made to determine the critical potentials required to produce various effects in gases, and in order to compare the results with other investigations, some of the values that have been obtained for argon and hydrogen may be considered. Prof. Horton and Miss Davies* have deduced from their experiments with argon, that the minimum ionizing potential V_1 is $15\cdot 1$ volts, and the minimum potential V_2 required to excite radiation is $11\cdot 5$ volts, and that ionization or radiation does not always occur when electrons collide with molecules with velocities corresponding to these potentials, but the proportion of the total number of

* F. Horton and Miss A. C. Davies, Proc. Roy. Soc. A. vol. xcvi. pp. 1, 27 (1920).

collisions with the larger velocity in which ionization takes place is increased when radiation is excited by a large number of collisions with the smaller velocity.

In these experiments the electrons that collide with the molecules are emitted by a hot filament, and the emission current may be of the order of a milliampere. A large proportion of the molecules in the path of the stream of electrons emitted by the filament may therefore receive several impacts per second from electrons moving with velocities greater than that corresponding to the potential V_2 , and it is possible that the ionization which is attributed to collisions with the velocity corresponding to V_1 is principally due to the ionization of molecules which had been affected by previous collisions. As the intensity of the stream of electrons from the filament is not stated in the published account of these researches, it is not possible to estimate the probability of ions being generated when an electron collides with a molecule in its normal state.

These experiments therefore do not show definitely that an appreciable number of molecules are ionized by collisions where the velocity of the electrons corresponds to 15.1 volts when a small current is passing through the gas, as in cases where the stream of electrons is measured by an electrometer, and it is impossible to estimate, from the value obtained for V_1 , the number of ions generated per centimetre by an electron moving through a gas under a constant electric force.

Some information as to the probability of electrons losing all their kinetic energy in collisions with the velocity corresponding to V_2 may be obtained from the experiments on the motion of electrons in gases. In argon when a stream of electrons moves through the gas at 20 millimetres pressure under a force of 25 volts per centimetre, the mean energy of agitation attains a value corresponding to 12 volts, and the ratio of the mean loss of energy of an electron in a collision with a molecule to the mean energy of agitation is 3.5×10^{-5} . Thus the proportion of collisions with velocity corresponding to 11.5 volts in which electrons lose all their energy is less than one in 10^4 . These experiments on the velocities of electrons in argon lead to the conclusion that, in general, electrons do not lose the greater part of their energy in collisions with normal molecules with velocities less than that corresponding to a potential of about 17 volts.

The value of the minimum potential V_1 required to ionize a molecule of hydrogen, V_2 to excite radiation in a molecule, and V_3 to dissociate a molecule given by F. Horton and Miss A. C. Davies, are $V_1 = 16.9$ volts, $V_2 = 13.9$ volts, and

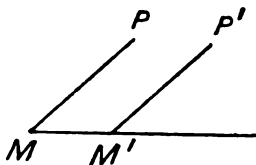
$V_3 = 2.5$ volts. When a stream of electrons moves through hydrogen under a constant electric force X_0 , and each electron makes several collisions with molecules of the gas in passing through a distance of the order V_1/X , the number of ions generated by collisions would be extremely small if the electrons lost the greater part of their energy in collisions with velocities greater than 2.5 volts. The experiments that have been made on the motion of electrons in hydrogen show that the ratio λ of the mean loss of energy of electrons in collisions with molecules, to the mean energy of agitation of the electrons, increases continuously with the velocity of agitation, the values of λ being 4.5×10^{-3} , 9×10^{-3} , and 25×10^{-3} for the velocities of agitation corresponding to one volt, 2.5 volts, and 4 volts respectively. Thus when collisions occur with velocities considerably greater than that corresponding to 2.5 volts, the average loss of energy is a small fraction of the kinetic energy of the electron. These experiments show that if molecules of hydrogen are dissociated by electrons moving with a velocity corresponding to 2.5 volts, it is only in a small proportion of the total number of collisions that dissociation occurs.

XLIX. *Suggestions regarding an Alternative Theory.*

By C. H. BICKERDIKE*.

ACCORDING to the classical conception of Faraday lines, the existence of matter affects the state of the æther in some degree, however small, at any distance from the matter. In that respect there is an important difference between the relation of matter to the æther and the relation of a body floating in water to the water.

When matter is in uniform motion, the Faraday lines are carried along with it—i. e., the state of the æther at any point at any distance from the matter is being altered. If the matter is at one moment at the point M, the æther is in a certain state at a point P. When the matter has arrived at M', the state of the æther which was formerly found at P is now found at P'. In Relativity theory the same idea is expressed by saying that matter affects the state of "space" and this state moves as the matter moves. It



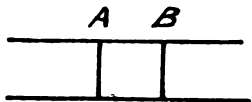
* Communicated by the Author.

is very important to remember, however, that the essential point about the Faraday line conception is that the state of the æther is differentiated particularly along the direction MP. It is not merely that there is, around P, in all directions equally, some difference of state in the æther due to the existence of the matter at M. There is some special significance in the linear direction PM.

The writer prefers to speak of æther rather than of space, since it is admitted that Einstein's "space" is not mere emptiness, but something having properties and capable of being the vehicle of forces. The æther may not be exactly "matter," but it is something which has relations to matter and can interchange energy with matter.

The theory that the existence and the motion of matter imply effects upon the state of the æther at all points distant from the matter has an important bearing on the theory of propagation of wave-motions.

If a sound-wave is started from a vessel floating in or immersed in water, there is no reason for supposing that the state of the water at a distance from the vessel is affected by the existence of the vessel or by its uniform motion in any manner which has a bearing on the velocity of propagation of sound. The principle that the velocity of the sound-wave depends only on certain properties of the medium can be established by imagining the medium to be contained in a tube and taking cross-sections at A and B. The



tube is imagined to move with a velocity in the direction opposite to that of the waves, so that the same phase of the wave is always found at A, say a crest or maximum compression, and at B always a hollow or maximum of rarefaction. The supposition is that the state of the medium at A and at B remains constant; and on that supposition it is demonstrated

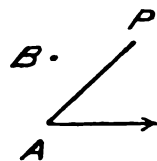
that the velocity $u = \sqrt{\frac{E}{\rho}}$ and is independent of the length of the waves and of the strength of the impulse which started them.

If we now consider the case of waves in the æther—it is immaterial to the point in question that they are transverse, and not longitudinal—propagated from a body which itself has a velocity v , then in order to get the same conditions, that the states of the æther at A and B are constant, we should have to attribute a velocity of $v+c$

to the tube if we are regarding the matter from the point of view of an observer who was not sharing in the motion.

It does not follow that there would be any means of measuring that velocity from an outside point of view. Perhaps all that we are entitled to infer is that the velocity of light should appear constant from point to point on the moving system, to observers on that system.

If light is being emitted by two bodies, A and B, and A has a velocity V in the direction of the arrow, and B is stationary, and if we consider any point P distant from both of them, the Faraday line conception would lead to the conclusion that light travelling along the direction AP from A would have velocity C plus the motion of the line AP, but light travelling along BP need not be affected in anything like the same



degree by the fact that the state of the æther along the line AP is in motion. We should expect only that the facts that the matter A exists and that it is in motion, by making the state of the æther at P not quite identical with what it would otherwise be, would have some kind of effect upon radiation emitted by B and passing through P. The existence of A implies a gravitational field, and it is not unreasonable to suppose that this is intimately related to the Faraday lines. The bending of light on passing through a gravitational field may be the effect caused by the mere existence of A and its lines on the light travelling along the direction BP. There may be also a further effect if the gravitational field and the lines are in motion.

The connexion between Faraday lines and gravitation, and the apparent similarity of gravitational attractions and centrifugal forces due to rotation, will be referred to again later. Something has to be said first, however, on the question whether the theory suggested is in accordance with observed facts, such as Majorana's experiments. The question of Aberration is dealt with later.

The Michelson-Morley Experiment and the Lorentz Transformation.

On the supposition that light is transmitted at constant velocity through a stationary æther, the distance traversed by the light at right angles to the earth's motion is $\frac{2l}{1 - \frac{v^2}{c^2}}$,

and that traversed by the light in the direction of the earth's motion is $\frac{2l}{\sqrt{1-\frac{v^2}{c^2}}}$, v being the velocity of the earth.

On the theory which the writer suggests, the two distances would both be equal to $2l$ measured along the earth's lines, because the Faraday lines belonging to the earth partake of its motion, and the light travels along those lines with a velocity constant relative to them. But if one take the standpoint of a spectator on the sun, the velocity of the light along the direction of motion of the earth is $v+c$ one way and $v-c$ the other way.

That is not to say, however, that the spectator stationary relative to the sun would have any easy way of measuring these velocities. We cannot measure the velocity of light in a direct manner analogous to the measurement of the velocity of sound.

The Lorentz transformation is obtained by assuming that the velocity of light must be made to be constant, and equal to c only, in each direction. That necessitates that the length along the direction of motion must be regarded, from the point of view of an observer not sharing in the motion, as contracted, and that a corresponding change in the measurement of time is made. This only means, however, that the results, so far as regards observations made entirely from the origin of axes, are *as if* the lengths were contracted and the times varied in accordance with the formulæ.

The actually observed results of measurement of the velocity of light are, as a matter of fact, too inexact to furnish any certain conclusion that the velocity is constant as measured when the light is reflected back to the one observer. Assuming, however, that this constancy is observed, it can be accounted for on the theory above suggested; and the Lorentz transformations are then to be regarded as merely fictitious devices for expressing the truth in a way which may have some conveniences, but without meaning that the lengths of material bodies and the motions of clocks are, in any real sense, varied in accordance with the transformation of x and x' and of t and t' .

If we consider Einstein's train and the platform, so long as an observer on either of these confines his experiment to light produced on his own system and reflected from mirrors or passed through lenses all on his own system, it may be

believed that he will find the velocity of light constant even if the measurement is made by two observers at a distance from one another. The Faraday line theory would account for that. It is not so obvious, however, what we should suppose would be the case on relativity principles if the light were reflected from one system to the other.

Suppose we have an observer S at the rear end of the platform and another S' at the rear end of the train, and each produces a flash of light at the moment when the observers are adjacent to one another.

Taking the observer S, on the platform, he is supposed to "judge" that the front end of the train only reaches to a point P on the platform. He has at P a mirror which reflects part of the beam back to S. Another part is reflected across to the train (a very short distance). At the moment when the light reaches P, a part of the train not quite at the front end will be opposite P, say P', where there is a mirror which reflects the light back to S. Another part of the beam from S goes direct to P' and is reflected back to S.



Would a toothed-wheel arrangement at S show all these three beams as having the same velocity as judged by S?

We certainly do not know experimentally that this would be the case. Possibly a test might be made by a toothed wheel (or two such wheels adjacent and revolving in opposite directions), the light being reflected back from a great distance in two beams, one from a fixed mirror and one from one of Majorana's rapidly revolving mirrors adjacent to the fixed mirror.

Even so, however, it might be the case that mere transmission through the air would involve loss of any velocity imparted by the revolving mirror.

Indirect inferences from interference are of doubtful import, as may be seen from the following observations on Majorana's experiments.

Majorana's Experiments.

Majorana's well-known experiment, designed to test whether a ballistic theory of the propagation of light is tenable, is described in the *Phil. Mag.* 1918, pp. 163-174.

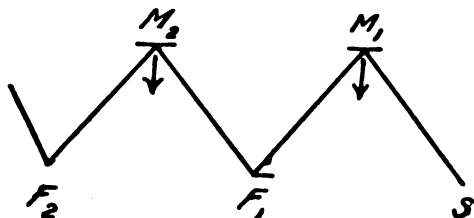
It may be decisive against a simple emission theory which regards light as a stream of projectiles which, on reflexion from mirrors, behave like elastic particles rebounding. It is submitted, however, that the conclusion that the velocity of light is always constant relative to the observer does not necessarily follow. There is an alternative conception which would equally well fit in with the results of the experiment: namely, that the light is propagated along the Faraday lines which belong to and are at rest relatively to the body from which the light proceeds, including the case of reflexion from a mirror, and that the velocity of propagation is constant relative to those lines which themselves have the translatory motion, if any, of the body to which they belong. Relative to the observer, the velocity of propagation would, on this theory, not be equal to c , relatively to a stationary observer, when the light was reflected from a moving mirror; it would be reflected with a velocity $c \pm v$ (according as the mirror was moving towards or away from the observer). In this respect the theory resembles the ballistic theory, but the important difference between the two occurs when that light is again reflected from a fixed mirror. On the ballistic theory, the light reaching the fixed mirror with velocity $c+v$ would be reflected with this velocity and the wave-length would not be altered. On the Faraday line theory, however, the light, though arriving at the stationary mirror with velocity $c+v$, would leave it with velocity c , and the wave-length would necessarily be reduced. On the other hand, if it arrived with velocity $c-v$, and left with velocity c , the wave-length would be increased.

In Majorana's experiment the wave-length would be reduced at each reflexion from the *fixed* mirrors when the moving mirrors were moving towards the source of light, and the reduction would be additive for each such reflexion. The result would be exactly the same as on Majorana's own theory, only the points at which contractions of wave-length would occur would be at the fixed instead of the moving mirrors.

Similarly, on the reversal of the motion, there would be increases of wave-length at each reflexion from the fixed mirrors.

Another possible view is that the light might be supposed to travel along the Faraday lines belonging to the body *on to* which the light was falling. This would operate in substantially the same way as on the previous supposition.

Let S be the source of light, M_1 and M_2 mirrors moving in the direction indicated by the arrows with velocity v resolved along the direction of the lines M_1S , M_1F_1 , and M_2F_2 . F_1 and F_2 are fixed mirrors.



1. First suppose transmission along the lines *from* which the light is proceeding. The line SM_1 is then stationary. The wave-length is λ , as judged by a stationary observer if he were able to observe it, and the velocity of transmission along SM_1 is c . Owing to the motion of M_1 , there would be, *for an observer on M_1* , a Doppler effect, apparently contracting the wave-length, but the light would be reflected along the line M_1F_1 , which would have velocity v , and the light would have velocity $c+v$ towards F_1 . The wave-length would still be λ along M_1F_1 . The light is then reflected along F_1M_2 with velocity c , and the wave-length is reduced to λ' and is still λ' on reflexion along M_2F_2 , and is again reduced further on reflexion from F_2 .

In this diagram the mirrors are represented, for simplicity, as all parallel to one another, and the angle of incidence is uniformly the same at each mirror. It is not a picture of Majorana's apparatus.

2. Suppose transmission is along the lines belonging to the system *on to* which the light falls.

The wave-length along the line SM_1 , which is moving towards S with velocity v , will now be λ' , and the light will travel, relatively to S with velocity $c-v$. It will be reflected along M_1F_1 with velocity c , but the wave-length will not be increased, because the number of waves falling on M_1 per unit of time will be the number emitted by S , say N . That number will be transmitted along M_1F_1 with velocity c , but they will be crowded in just the same way as along SM_1 . A further crowding will occur along F_1M_2 .

The result of the second experiment appears also to be in accordance with either of these theories. The light, before reaching the eye, is reflected from a stationary mirror. On

the supposition that it is carried along the Faraday lines of the moving source, the wave-length is not reduced by the motion; but on being reflected from the stationary mirror, along the lines of that mirror, the velocity would be c only and there would be a reduction of wave-length. The net result, on reaching the eye, would be the same as if transmission had been all the time through a stationary æther.

On the supposition that transmission is along the lines of the recipient body, the reduction of wave-length would occur at the point of emission, and the result would also be the same as in the case of transmission through a stationary æther.

The discussion in terms of Faraday lines does not, of course, give us any simple physical picture of the æther and of what is happening in it. The æther remains as mysterious as ever, but, it is submitted, not more mysterious than Einstein's "space."

L. A *Determination of the Coefficient of Reflexion of X-Rays for Calcite and Rock-Salt.* By BERGEN DAVIS, *Professor of Physics, Columbia University, New York,* and H. M. TERRILL*.

WHEN a beam of X-rays, after reflexion from a crystal surface, falls on a second crystal, maximum reflexion is obtained when the planes of the two crystals are parallel. Nevertheless, some reflexion is observed when the second crystal is rocked through a small angle each side of the position of parallelism. This indicates that when a beam of non-homogeneous X-rays falls on a single crystal, not only is there reflexion of the rays of wave-length λ , corresponding to $\lambda = 2d \sin \theta$, but some energy of neighbouring wave-lengths is also reflected. The amount of associated reflexion, as indicated by the width of the rocking curves, depends on the nature of the crystal, the perfection of its crystalline structure, and the condition of the surface. This fact introduces some difficulties in specifying the reflectivity of a crystal.

W. L. Bragg † has defined a quantity which he calls the coefficient of reflexion, and he has determined the value of this coefficient for rock-salt. A similar quantity has been defined by A. H. Compton ‡, and determined for rock-salt and also for calcite.

* Communicated by the Authors.

† Phil. Mag. Jan. 1921 and July 1921.

‡ Phys. Rev. July 1917.

In both cases the expression taken as the coefficient of reflexion is $R = \frac{E\omega}{I_0}$, where E is the total deflexion of the electrometer as the crystal is rotated with an angular velocity ω through an angle covering the wave-length in question, and I_0 the deflexion when the direct beam is allowed to enter the ionization chamber for one second. This expresses the coefficient of reflexion in terms of angle, Compton giving it per degree and Bragg per radian.

It is understood that the beam of X-rays used is in all cases monochromatic, being either a prominent characteristic line of the target used, or a narrow range selected from the general radiation by previous reflexion on another crystal.

Bragg states, as justification for his definition of the coefficient of reflexion, that this quantity makes allowance for the imperfection of the crystal and gives an integrated or average result that will depend on the nature of the crystal and not on its state of perfection.

It is one of the purposes of this paper to show that the coefficient of reflexion is not independent of the crystal surface, but depends greatly on the perfection of this surface.

Investigations of the reflectivity of calcite and rock-salt have been recently completed by Bergen Davis and W. M. Stempel*, using a specially constructed double spectrometer. In these investigations the general radiation passing through the slits fell on the first crystal designated as crystal A. The reflected radiation from this crystal then fell on a second crystal designated as B, and the radiation reflected from B was measured by an ionization chamber in the usual manner.

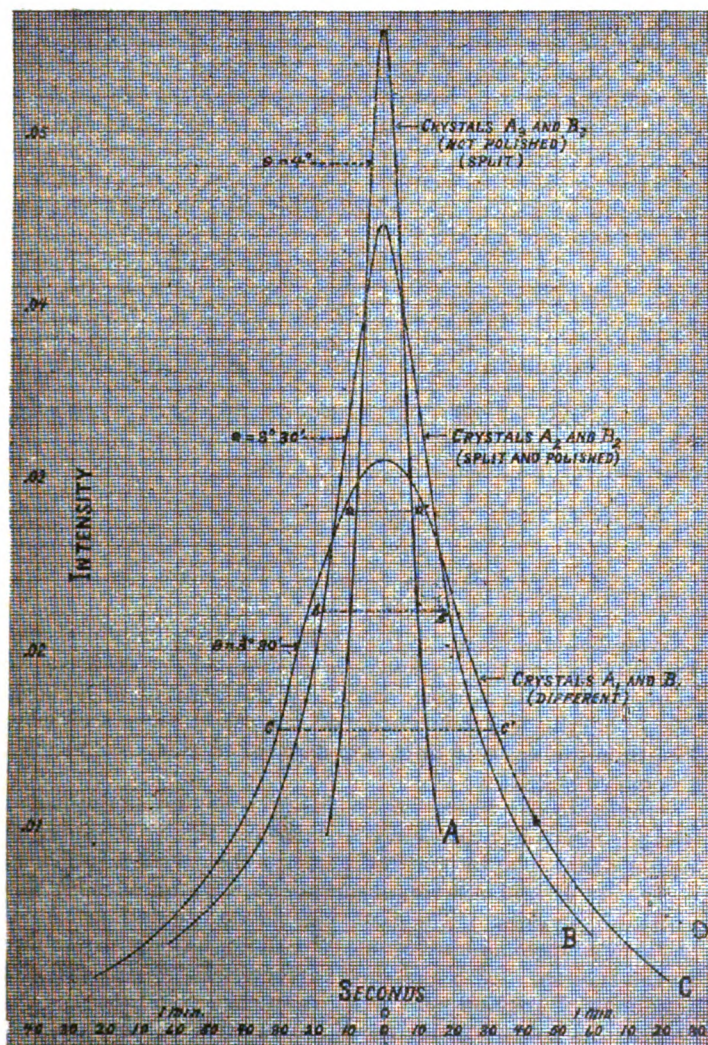
Maximum reflexion was obtained when the crystal planes were parallel, and the curves of intensity called rocking curves were obtained when crystal B was turned on each side of the position of parallelism (see fig. 1). Crystal B was so arranged that it could be moved aside and the beam from A allowed to enter the ionization chamber directly. The ratio of the two intensities, that reflected from B at parallelism over that reflected from A, was expressed in percent and called the percent reflexion. This was taken as a measure of the reflectivity of the crystal.

The results of Davis and Stempel can be expressed in terms of the coefficient of reflexion as defined by Bragg

* Phys. Rev. May 1921 and May 1922.

and Compton, and a direct comparison can be made. Each determination of Davis and Stempel consists of a rocking

Fig. 1.—Rocking curves for Calcite.



curve, *i. e.* a curve of intensities at angles close to that of parallelism, and an observation of the intensity of the beam reflected directly from the first crystal. In practice,

Phil. Mag. S. 6. Vol. 45. No. 267. March 1923. 2 H

the intensities were measured by recording the time required for a unit electrometer deflexion, but the quantities plotted were the reciprocals of these times, giving the deflexions produced in one second.

A rocking curve then is a curve whose abscissæ are angles and whose ordinates electrometer deflexions, or, what is the same thing, intensities. To obtain the coefficient of reflexion from the rocking curve, suppose the axis of abscissæ divided into equal intervals $\Delta\theta$, and that the unit of angular magnitude selected (in this case, one degree) contains m such intervals. Further, draw an ordinate of the curve at the centre of each division, and call the sum of all these ordinates ΣI .

Then, if $\Delta\theta$ is small, the expression $\Sigma I \Delta\theta$ will give the area under the curve. But ΣI corresponds to the total deflexion of the electrometer if the crystal had been rotated with an angular velocity $\frac{1}{m}$, since ΣI is the sum of electrometer deflexions and $\frac{1}{m}$ gives the number of degrees passed over per second; whence $\Sigma I \cdot \frac{1}{m} = E\omega$.

We have then

$$\frac{E\omega}{I_0} = \frac{\Sigma I \cdot \frac{1}{m}}{I_0} = \frac{\Sigma I \Delta\theta}{I_0 m \Delta\theta}.$$

Now the fraction on the right is readily obtained from the rocking curves of Davis and Stempel, by dividing the area under the rocking curve by the area of a rectangle whose height is the intensity of the direct beam and whose length is the angular unit, one degree, on the scale to which the curve is drawn.

Hence, to obtain the coefficient of reflexion as defined by Bragg, it is only necessary to measure the area under the curve with a planimeter and perform the division indicated.

In the case of calcite, observations were made with three pairs of crystals. The first pair is designated as A_1 - B_1 . A_1 was a specimen of Montana calcite, having slight flaws in the interior and a polished surface. B_1 was an old clear specimen of Iceland spar with its surface polished.

For the second pair, A_2 - B_2 , a crystal of clear Iceland spar was split, the surfaces polished, and the crystal mounted so that the reflecting surfaces were planes that had been in contact before splitting. The third pair, A_3 - B_3 , was also obtained by splitting a clear crystal of Iceland spar. The

freshly split surfaces were not polished, and all contact with them was carefully avoided during the process of mounting. As mounted, the two reflecting surfaces were the contiguous planes before splitting.

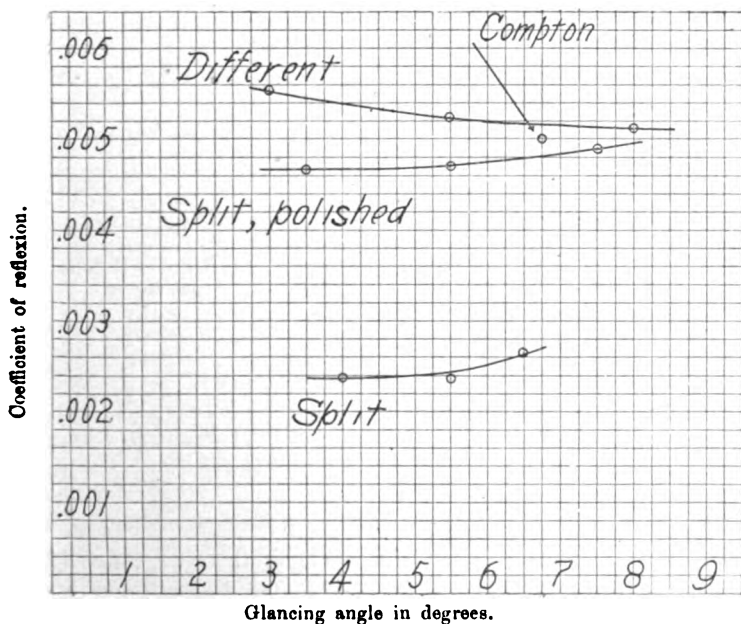
The three pairs showed marked differences in reflectivity and width of the rocking curves. The results obtained are given in the following table and are also exhibited in the curves (fig. 2).

Calcite.

Crystals.	Glancing Angle.	Percent Reflexion.	Coefficient of Reflexion per degree.
A ₁ -B ₁	3° 0'	25.8	.00552
	5° 30'	20.8	.00523
	8° 0'	17.3	.00512
A ₂ -B ₂	3° 30'	35.4	.00466
	5° 30'	29.2	.00470
	7° 30'	25.3	.00489
A ₃ -B ₃	4° 0'	44.4	.00238
	5° 30'	43.1	.00238
	6° 30'	42.8	.00265
Compton	6° 45'		.0050

Fig. 2.

Coefficient of reflexion for Calcite for different glancing angles



The value of the coefficient for the dissimilar polished crystals, A_1-B_1 , agrees with that obtained by Compton.

It will be observed that the coefficient obtained for the more perfect pair, A_2-B_2 , is about one-half of that obtained for the pair A_3-B_3 . Both these pairs were split crystals, the only difference being that the surfaces of the pair A_2-B_2 were polished. Evidently the act of polishing has doubled the coefficient of reflexion.

The table further shows that the coefficient decreases with increasing wave-length for the pair of dissimilar crystals, but that it increases slightly for the two more perfect pairs. Fig. 1 is reproduced from the original paper, and shows rocking curves for the three different pairs of crystals. Attention is called to the extreme narrowness of these curves, in particular for the case of crystals A_3-B_3 .

A similar investigation of the reflectivity of rock-salt has been also made by Davis and Stempel. Two sets of rock-salt crystals were employed. They were split and mounted in the same manner as the calcite. Experiments were made both with freshly split surfaces and with polished surfaces, but it was found that polishing did not have a marked effect on the reflectivity.

The rocking curves obtained were somewhat irregular and quite wide, being more than fifty times as wide as the narrowest curves obtained with calcite. However, the curves obtained were not as wide as that found by Bragg for an unpolished crystal.

The curves were integrated, and the coefficient of reflexion is given in the following table :—

Rock-Salt.

Crystals.	Glancing angle.	Percent reflexion.	Coefficient of Reflexion per degree.
Split	3°	24.8	.0480
	5°	15.3	.0294
	7°	13.0	.0214
Washed and polished .	3°	22.1	.0462
	5°	15.1	.0309
	7°	11.5	.0231
Compton.....	7° 15'		.023
Bragg	6° 15'		.031

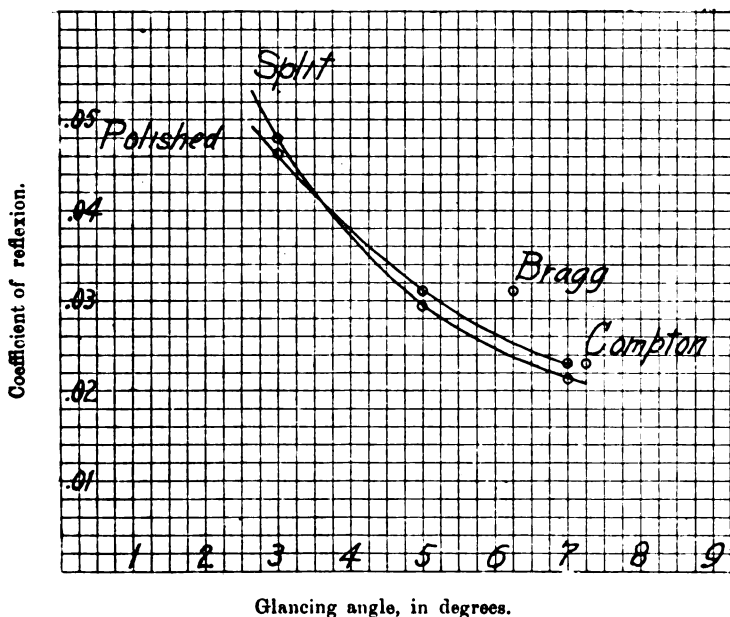
The value listed for Bragg is his final value, taken from the Phil. Mag. July 1921, p. 7, and the angular units changed from radians to degrees by multiplication by 57.3.

The comparison with the values of Bragg and Compton is also exhibited graphically in fig. 3.

The results indicate that the crystal used by Compton was of about the same quality as those of Davis and Stempel, while that of Bragg had a much poorer surface, as evidenced by the higher coefficient obtained and also independently by the wider rocking curve. It is interesting to note that the coefficient of reflexion increases sharply with decreasing

Fig. 3.

Coefficient of reflexion for Rock-Salt for different glancing angles.



wave-length. It would seem that an increase in this direction is characteristic only of crystals of imperfect surfaces, since we find a decrease for perfect calcite, a slight increase for the imperfect calcite, and a sharp increase for rock-salt, which is always far more imperfect than calcite.

In general, a comparison of the reflectivities of rock-salt and calcite cannot be made directly. Rock-salt has a low, wide rocking curve, whose large area gives a high coefficient of reflexion, while the curve for calcite is high and narrow, having smaller area but greater percentage intensity at the

maximum. To say which substance is the better reflector depends entirely on the point of view. Furthermore, in both cases the reflectivity is dependent on the perfection of the crystal surface, a rough surface increasing the width and area of the rocking curve but diminishing its height.

We seem driven to the conclusion that there is no single quantity which can be properly used as a measure of the reflectivity, and that to completely specify the reflecting power of a substance requires the determination of two constants.

One of these might well be the coefficient of reflexion as used by Bragg. Since this involves both the area and height of the rocking curve, the selection of the second quantity becomes rather difficult, if it is desired to have the pair simply related to the fundamental constants of the curve. As simple a selection as any is to take as one of the two required quantities the width of the rocking curve, either at half maximum, or at the points of inflexion, and as the other, the ratio of the reflected to the incident intensities, or the percentage reflexion.

Phoenix Physical Laboratories,
Columbia University.

Note added Nov. 20, 1922.

Since the above was written, there has come to our attention an article by Wagner and Kulenkampff* giving values of the coefficient of reflexion for calcite and rock-salt for longer wave-lengths.

They find for calcite .0046 per degree at 1.54 and 1.75 Å. Assuming the coefficient for calcite to be approximately independent of the wave-length, we take this value to indicate that the crystal used was of about the same degree of perfection as our A_2 - B_2 .

For rock-salt they obtain .0157 per degree at 1.54 Å and .0145 at 1.95 Å. These values show that the decrease in the coefficient with increasing wave-length that we observed for short wave-lengths still holds at the longer wave-lengths.

Incidentally they mention a remark of Küstner† that in the original observations of Davis and Stempel the voltage employed was so high as to cause overlapping of the second order at the longer wave-lengths. This is an error; the voltage was always kept low enough to prevent second order from being present at the wave-length used.

* *Ann. d. Phys.* xiii. (1922).

† *Zeitschr. f. Phys.* vii. (1921).

LI. *On the Longitudinal Elasticity and Poisson's Ratio of India-rubber.* By G. B. DEODHAR, M.Sc., Assistant Professor of Physics, Muir Central College, Allahabad*.

Introduction.

THE case of india-rubber owes much of its interest to the peculiar behaviour which it evinces when the operating load is put under different conditions of the substance. So far practically nothing is known of the constitution of india-rubber. A very intelligent attempt was made by Mr. Ono † to hit at a probable constitution of the substance by arriving at a theoretical formula for stress and strain, on certain assumptions, which would satisfy his experimental observations. But the very fact that he had to modify it to some empirical form points against his assumptions. It is most probably the extreme complexity of the constitution of india-rubber which is responsible for its striking behaviour at different temperatures and under various strains. The inversion temperature observed by A. E. Lundal ‡, the relation between elasticity modulus and temperature investigated by G. R. Dallander § and A. E. Lundal ||, the elastic after-effect experimentally studied by J. C. Shedd and R. L. Ingersoll ¶, and the relation between elongation and time for a particular pull investigated by P. Phillips** are some of the most interesting phenomena which are expected to throw some light on the molecular composition of india-rubber. However, it seems that very little has been done with a view to study experimentally the variation of the modulus of longitudinal elasticity with stretching. It is also very interesting to study whether in the face of varying modulus with stretching force Poisson's ratio really remains constant. A full study of these two phases of elastic strains in india-rubber would be a valuable help in the establishment of reliable elasticity equations. The present experiment was undertaken to study the elongation of india-rubber from the beginning of a finite strain up to the breaking point of the sample. It was also thought worth while to study Poisson's ratio over the whole range.

* Communicated by the Author.

† Proc. of Tokyo Math. Soc. vol. vii. (1913).

‡ Wiedemann's *Ann.* Dec. 1898, p. 741.

§ *Ofvers af Vet.-Ak. Forh.* xxviii. p. 703 (1871).

|| *Loc. cit.*

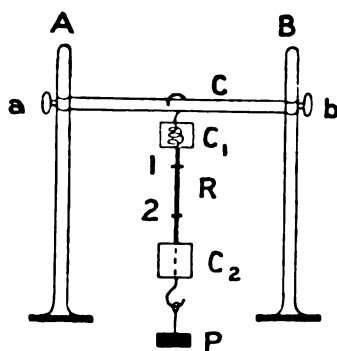
¶ *Phys. Rev.* xix. pp. 107-116, Aug. 1904.

** *Phil. Mag.* ix. pp. 513-531 (1905).

Experimental Arrangement.

The experimental arrangement is shown in the diagram, fig. 1. A and B are strong iron stands; C is a horizontal iron bar clamped to A and B at *a* and *b*. C_1 and C_2 are small brass frames with corrugated grooves to hold the rubber piece R very firmly. P is a small weight-pan hung from a hook at the bottom of frame C_2 . The whole suspension is suspended from the transverse bar C by a hook at the top of frame C_1 . By putting weight on pan P any amount of tension could be applied to the rubber sample. The samples selected were pieces from rubber cords of circular cross-section. The diameter of the cross-section was obtained by

Fig. 1.



A & B, massive iron stands; *a* & *b*, clamps; C, a cross-bar of iron;
 C_1 & C_2 , brass frames to clamp rubber band R; P, weight-pan.

taking the mean of several observations along the length of the cord. The measurements were made by a fine screw gauge reading up to 0.001 cm. Two fine marks 1 and 2 were made on the length of the cord, and the distance between the two was measured by a cathetometer kept at a distance. The distance between these two marks gave the length of a certain portion of the cord under various loads. The cathetometer could read up to 0.01 cm. As stretching under a definite pull is a function of time, the length corresponding to a particular load was measured some definite time after the application of each load. The temperature of the substance was 23.0°C. and remained constant throughout the experiment. Any other sample could be substituted in place of the previous one simply by unscrewing the frames C_1 and C_2 . The lengths were measured for increasing loads only, the observations being carried on up to the breaking point.

Observations and Discussion of Results.

A certain length of an old rubber cord was cut out and suspended as described above. The following table gives the cross-section and length of the sample corresponding to each load up to the breaking point.

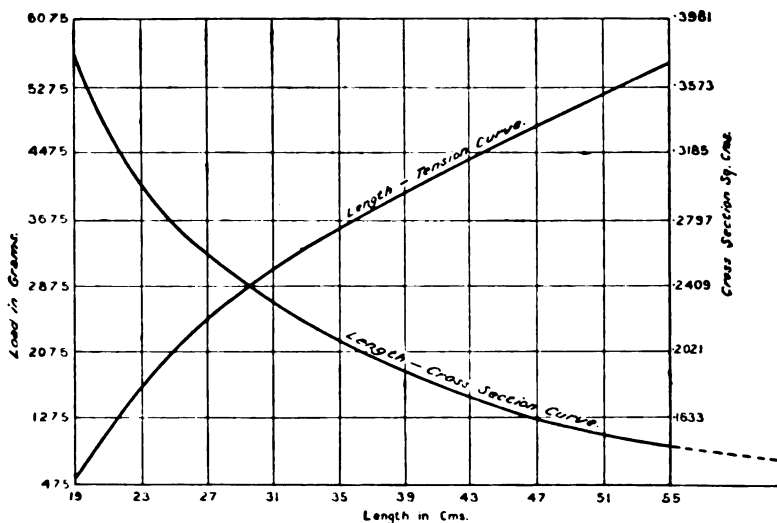
TABLE I.

Load.	Cross-section.	Length.
520 gms.	0.3771 sq. cm.	19.25 cms.
560 "	0.3692 "	19.38 "
600 "	0.3661 "	19.48 "
820 "	0.3524 "	20.12 "
970 "	0.3435 "	20.72 "
1120 "	0.3350 "	21.23 "
1320 "	0.3290 "	21.94 "
1520 "	0.3193 "	22.74 "
1720 "	0.3087 "	23.58 "
1920 "	0.2859 "	24.54 "
2120 "	0.2824 "	25.66 "
2320 "	0.2649 "	26.83 "
2520 "	0.2545 "	28.04 "
3020 "	0.2358 "	31.14 "
3520 "	0.1988 "	35.94 "
4020 "	0.1801 "	39.85 "
4520 "	0.1639 "	44.66 "
5020 "	0.1536 "	49.87 "

These observations were plotted on one graph paper and two curves, viz., length-tension curve and length-cross-section curve, were obtained (fig. 2). From the diagram it is seen that the cross-section of the material goes on decreasing logarithmically as the length increases. A close scrutiny of the length-tension curve shows that up to a point where the stretched length is about $5/4$ times the original length a linear relation between length and tension holds good. Then, after that, there is a bend till the stretched length attains about twice the original value; after that, up to the breaking point a linear relation holds good again. The angles which the two linear portions make with the axis of lengths are different. From the inclinations of the lines it can be seen that over the range where the second linear relation holds good, a certain amount of load produces a greater elongation than that produced by the same load over the range where the first relation holds good. The second linear relation is more conspicuous than the first one as its range is larger.

The specimen was then taken out of the frames and another specimen was put in its place. This specimen was a certain length out of a new india-rubber cord. Observations

Fig. 2.



on this were taken in the same way as observations taken in the previous case. The general characteristic of the two curves are the same. For convenience I give below (Table II.) observations from 3000 grs. load and onwards up to the breaking point.

TABLE II.

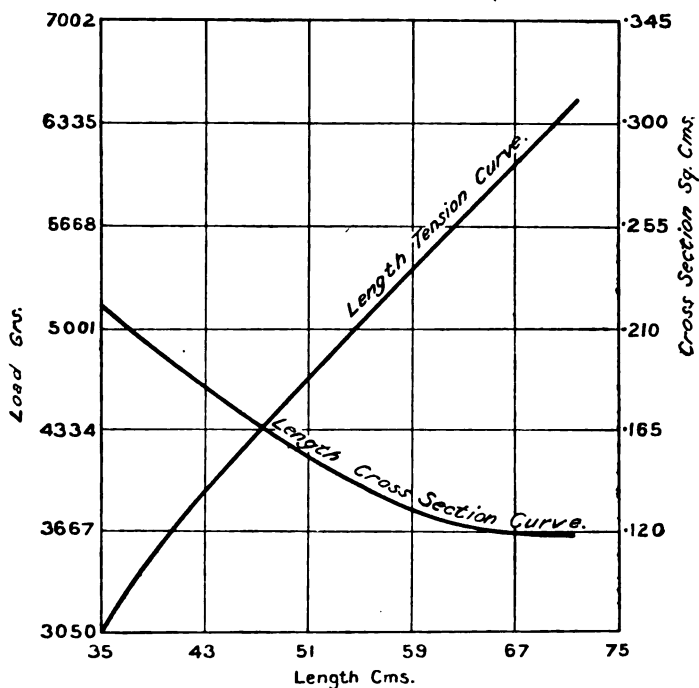
Load.	Cross-section.	Length.
*		
3000 gms.	0.2105 sq. cm.	34.89 cms.
3500 "	0.1949 "	39.07 "
3750 "	0.1900 "	41.01 "
4000 "	0.1800 "	43.84 "
4250 "	0.1670 "	47.02 "
4500 "	0.1597 "	48.91 "
4750 "	0.1520 "	52.20 "
5000 "	0.1479 "	54.82 "
5250 "	0.1390 "	57.61 "
5500 "	0.1341 "	60.16 "
5750 "	0.1300 "	63.20 "
6000 "	0.1280 "	65.88 "
6250 "	0.1220 "	68.81 "
6500 "	0.1204 "	71.70 "
6750 "	Broke	Broke

* Observations above this in original record.

The linearity after the bend is quite prominent in fig. 3.

In the case of india-rubber, unlike metals, any deforming force produces a finite stretching, and consequently the usual elasticity relations are not strictly applicable. However, if we take any two consecutive observations we should be fairly

Fig. 3.



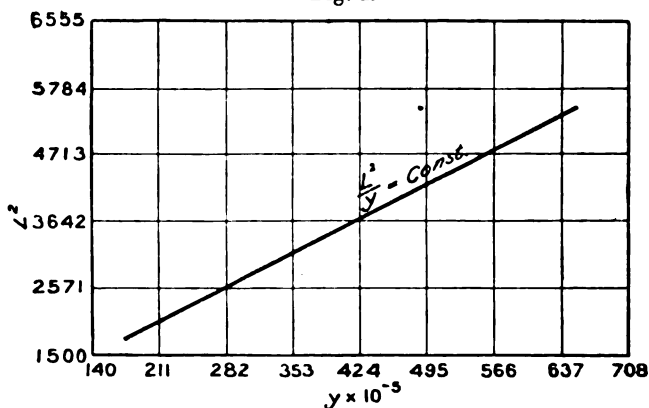
justified in applying Hooke's law. From Tables I. and II. values of Young's modulus were calculated, and it was found that the ratio of Young's modulus to the square of the stretched length over the two ranges where length-tension curve is a straight line, is a constant; while over the bend this constancy vanishes. The results for No. 2 are tabulated below.

TABLE III.

Stretched length L.	Young's modulus $y \times 10^{-5}$.	$\frac{L^3}{y} \times 10^3$.
39.07 cms.	149.9 dynes/cm. ²	0.098
41.01 "	152.0 "	0.091
43.84 "	182.1 "	0.094
47.02 "	222.0 "	0.101
48.91 "	243.6 "	0.102
52.20 "	280.0 "	0.103
54.82 "	280.5 "	0.093
57.61 "	360.0 "	0.108
60.16 "	402.2 "	0.111
63.20 "	452.0 "	0.113
65.88 "	492.9 "	0.110
68.81 "	550.0 "	0.116
71.70 "	611.0 "	0.118

From data in column 1 values of L^3 are calculated and these and data in column 2 of this table are plotted and the graph comes out to be a straight line (fig. 4).

Fig. 4.



This linear relation seems to be the most important feature of the elasticity of india-rubber, and any formula, theoretical or empirical, must bring out this relation in the initial and final stages of stretching. Mr. Ono * has obtained on certain assumptions the following theoretical formula :—

$$S_0 = A\lambda \left\{ 1 - \frac{2}{\lambda + \beta} \right\}, \quad \dots \dots (1)$$

where A is a constant, λ = length ÷ length in natural state

* Proc. Tokyo Math. Soc. vol. vii. p. 39 (1913).

and β = breadth $\div$ breadth in natural state. To suit his experimental observations he had to modify it to the following empirical form, which he says represents the relations between stress and strain very closely :

$$S_0 = A \left\{ 1 - \frac{2}{\lambda + \beta} \right\} \cdot e^{h(p-\lambda)^2}, \quad (2)$$

where A , h , and p are constants and S_0 stress upon original cross-section. Now there are certain facts which tend to show that both the above equations are of doubtful reliability. In the first place, as pointed out on p. 475, a deforming force produces finite stretching in this case, and so it would be erroneous to refer a load always to the original cross-section and length and breadth respectively always to those in the natural state as done by Ono. Secondly, substituting the values of S_0 , λ , and β in (1) should give us at least an approximate constant value of A . The following tables give the values of S_0 , λ , β , and A calculated from Tables I. and II.

TABLE IV.

S_0 .	λ .	β .	A .
3.7 $\frac{\text{kil. gr.}}{\text{cm.}^2}$	1.01	0.99	-731
3.9 "	1.01	0.98	-732
4.2 "	1.03	0.98	+844
4.6 "	1.04	0.98	442
5.1 "	1.06	0.98	249
5.4 "	1.09	0.97	171
5.8 "	1.11	0.95	100
6.5 "	1.14	0.95	100
7.3 "	1.19	0.93	107
8.1 "	1.25	0.91	87
8.8 "	1.31	0.88	79
9.6 "	1.36	0.86	70
11.5 "	1.52	0.83	50
13.5 "	1.75	0.76	38
15.3 "	1.94	0.71	31
17.2 "	2.23	0.69	24
19.1 "	2.43	0.68	22

Tables IV. & V. show that instead of being constant, A continually decreases with higher tensions. Substituting the values of A , λ , and β , we get a series of equations. Solving them by twos a number of values of h and p are obtained. It was found that there was no constancy in these values, showing that equation (2) is also not applicable. The

formulae thus fail to satisfy experimental observations and the relation, $\frac{L^2}{y} = \text{const.}$, does not come out of them.

Thirdly, a scrutiny of Ono's figures gives us that percentage discrepancy between the calculated and observed values of S_0 continually increases with higher tensions.

TABLE V.

(This table chiefly refers to the portion where $\frac{L^2}{y} = k$ holds.)

S_0 .	λ .	β .	A.
22 $\frac{\text{kil. gr.}}{\text{cm.}^2}$	1.13	0.98	324
25 „	1.26	0.95	208
28 „	1.41	0.88	121
3. „	1.57	0.84	116
35 „	1.72	0.82	95
37 „	1.88	0.79	78
41 „	2.05	0.77	68

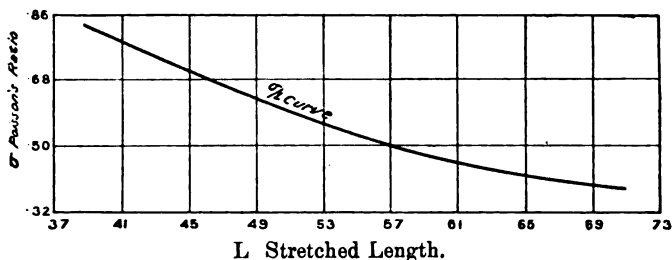
Poisson's ratio can be very easily calculated from data in Tables I. and II. It was found that this ratio is not a constant quantity but goes on decreasing with increasing length of the specimen. Some calculations are tabulated below and the data plotted on fig. 5 to bring out the relation between stretched length and Poisson's ratio.

Stretched length.	Poisson's Ratio.
39.07 cms.	0.87
43.84 „	0.77
48.91 „	0.63
54.82 „	0.54
60.16 „	0.48
65.88 „	0.42
71.70 „	0.38

This phenomenon together with the relation $\frac{L^2}{y} = k$ are of considerable interest since they are likely to throw some light on the nature of india-rubber, and would thus go a great way in establishing a general relation between stress

and strain by a rigorous mathematical treatment. The author hopes to obtain a general formula for elongation of india-rubber based on the theory of probability.

Fig. 5.



Summary.

In these experiments long and thick specimens were used. Variation of Young's modulus of india-rubber with load is experimentally studied, and it is found that there are two stages of stretching, initial and final, where $\frac{L^2}{y} = k$ holds good, L being stretched length and y Young's modulus. In the intermediate stages of stretching, that is during the changes where the length is between $5/4$ and 2 times the original length, the above linearity breaks down.

The author's experimental results are not correctly represented by the stress and strain formula of Ono. It is found that Poisson's ratio for india-rubber is not a constant quantity as is generally supposed, but decreases with increasing length of the specimen.

Another relation between stress and strain is necessary which will satisfy the above experimental observations, and the author hopes to obtain it on the basis of the theory of probability.

Muir Central College,
Allahabad, India.

LII. *Notes on the Radiation and Ionization Potentials of the Rare Gases and on the Singlet and Enhanced Series of Argon.* By W. M. HICKS*.

IN my recently published 'Analysis of Spectra,' I have discussed certain difficulties in connexion with the radiation and ionization potentials of hydrogen and the rare gases. Within the last few months the results of several important experimental investigations have been made known, which support the suggestions there made. In the following notes these are considered, the hypothesis made is more fully considered and extended, and an attempt is made to determine the various series in argon on which its potentials depend.

Radiation and ionization potentials are those through which an electron must fall, in order respectively to make a gas radiate or to ionize it. In general, such potentials must give sufficient energy to dissociate the molecule, and then to act on the atom at one operation. In what follows, the word "true" is used to indicate the potentials required to produce radiation or ionization in the atom, when this is in its radiating configuration. Thus the "observed" ionization potential should be the sum of the dissociation potential and the "true" ionization. The word is also used in an analogous way as explained below in the discussion of the potentials of the rare gases.

Hydrogen.

Rad.	$\left\{ \begin{array}{l} 10.5 \\ 14 \end{array} \right.$	Ion.	$\left\{ \begin{array}{l} 13.6 \\ 16.9 \end{array} \right.$	Dis-oc.	3.3
------	---	------	---	---------	-----

1. In hydrogen two sets of potentials are observed, the lower corresponding to the "true" values. How is it, that in the molecular gas H_2 , radiation and ionization can occur at their true or atomic values? In this case the true radiation (10.5) is about three times as large as the dissociation (3.3). Consequently, when the voltage has reached the true radiation value, each electron has sufficient energy to produce six atoms, any one of which may be made to radiate on impact by an electron possessing the full energy. But any such effect could not be recognizable unless the actual number of atoms present were an appreciable proportion of the whole gas. To explain this, it was supposed that the life of an atom, when formed, was long compared with ordinary molecular intervals—*e. g.* the life of an ion—but at that

* Communicated by the Author.

time there were no experimental data in support of the hypothesis. Since that was written, however, Wood * has produced evidence that an atmosphere of H takes about 1/5 second to change to H₂. This is an extremely long molecular interval, and should be sufficient to explain the persistence of a considerable proportion of H in an atmosphere of H₂ in which the electronic production of H per second just balances the recombination per second.

The Rare Gases.

2. In the rare gases the observed potentials are too large to represent the true values. No true voltages can be greater than those corresponding to N or 4N, according to the cases where the emitter is the atom or singly ionized (enhanced) atom. These voltages correspond to potentials of 13·54 and 54·16 respectively. Those of the gases hitherto observed—He, Ne, A—are considerably greater than these. This is not explainable by the existence of a dissociation potential, since here each molecule is already an atom. To meet this difficulty the suggestion was put forward that the ordinary atom in these gases is not capable of radiating in its normal condition, but requires some preliminary work to be done on it to change it into a configuration capable of emission. This supposition is supported also by the fact—at least proved in He—that the ordinary normal He atom does not absorb any of the He lines: in other words, it is not the actual emitter of these radiations. Further, it explains the absence of affinity between their own atoms or with those of other elements as due to the non-availability of their separable electrons. We shall indicate some evidence below that in Ne and A this change from the normal to the emitting states may take place in at least two stages. In discussing these gases it will be convenient to use symbols for these atomic configurations. We shall employ the following, in which a small dot represents a potential level, or position in the atom, a large dot an electron, and a - the nucleus :—

Normal atom	. ● - ● .
1st prepared atom ..	. ● - . ● or possibly ● . . . ●
1st ionized atom ..	. ● - . . , . ● . . .
2nd prepared atom ..	● . - . .
2nd ionized atom ..	. . - . .

* Phil. Mag. xlii. p. 729 (Nov. 1921).

Helium.

3. On the suppositions that the He radiation involved is $\text{HeP}''(1)$ —the strongest line,—and that the He^+ is that of $\lambda=1216$ or $4N(1/2^2-1/3^2)$, the values of the various voltages required were found to be

1st prel. to raise one electron to radiating state		20.8 volts
2nd prel. to raise the second, after 1st has been ejected	.	45.7 "
True radiation potentials		He=1.14; He ⁺ = 7.4 "
True ionization potentials		He=4.75; He ⁺ =13.5 "

or for observed values

Rad.:	He=20.8+1.14=21.9; He ⁺ =66.5+ 7.4=73.9 volts
Ion.:	He=20.8+4.75=25.6; He ⁺ =66.5+13.5=80 "

It will be noted that the work to bring up the second electron after the first has been ejected is more than twice that required to bring up the first; which is to be expected.

Experimentally, radiation is also observed at 20.8, the first preliminary voltage. This means that, as in the analogous case of H, there should be a very considerable number of prepared atoms present when this voltage is reached. Consequently, here also a very long life must be postulated for the prepared atom when produced. This postulate and the value of 4.75 for the true ionization, are now confirmed by some striking experimental results by F. Kannenstine*.

He studies the potential current curves in an alternating unidirectional arc in helium at different frequencies. When the frequency is small—about 60 cycles per sec.,—the arc strikes when the potential rises to 28 volts and dies out when it falls to about 4 volts. As the measures are not exact, it is clear that the first refers to the complete ionizing potential, *i. e.* prel.+ion., but that, as the voltage falls back, the prepared atoms subsist in sufficient number to enable the arc to run with voltages down to about 4 volts, when it ceases. In other words, the ionizing potential of a prepared atom is about 4, which, allowing for observation uncertainties, agrees with the estimate of 4.75 found above from spectral

* Astro. Journ. lv. p. 343 (1922). Kannenstine refers to an apparently similar modified atom proposed by Messrs. Franck, Reiche, and Knipping, but the present writer has not yet been able to refer to their original paper, published in the new German periodical, *Zeitschrift für Physik*.

considerations. If the frequency, however, is just over 220 cycles per second, the striking of the arc occurs at 4 volts, which Kannenstine explains by the life of the "metastable" atoms overlapping the time of a cycle; so that, when the potential again rises to 4 volts, there are sufficient prepared atoms still present to be ionized at 4 volts and to start the arc. The life must then be comparable with $1/220$ sec.—a very long molecular interval.

In a second set of experiments, in a continuous current arc at 35 volts the potential was suddenly reduced. If the reduced potential was less than 3·5, the current died out immediately; if just over, there were indications that it died out not instantaneously*. When the lower voltage rose to 22·6, the arc seemed to be maintained for a short time before dying out, and a further slight increase to 23·6 brought out another change in that the current died out in two steps. The first is clearly due to the persistence of prepared atoms. It may be suggested that the two steps are due to the two possible prepared atoms $\bullet\bullet\text{--}\bullet\bullet$ and $\bullet\text{--}\bullet\bullet\bullet$, the second requiring about 1 volt more than the first and having a shorter life. In the first continuance of the arc the current is carried by both forms; then $\bullet\text{--}\bullet\bullet\bullet$ quickly changes to $\bullet\bullet\text{--}\bullet\bullet$ or $\bullet\bullet\text{--}\bullet\bullet$, and in the second step the current is carried by $\bullet\bullet\text{--}\bullet\bullet$. In Kannenstine's work we thus have the first experimental proof of the existence of a specially prepared atom different from the normal, of long life, and with an ionization potential in the neighbourhood of 4 volts.

The enhanced radiation of 73·9 has not—so far as the writer knows—been specially noted by any observer. It may be well, therefore, to consider in more detail the processes going on after the first ionization potential has been reached. For simplicity we shall take the two electrons as equivalent in the normal atom. Above 25 volts there may be present $\bullet\bullet\text{--}\bullet\bullet$, $\bullet\bullet\text{--}\bullet\bullet$, $\bullet\text{--}\bullet\bullet\bullet$, and even He^+ ; but as the life of an ion is probably short, the number of He^+ would be comparatively small, and their effect on enhanced radiation negligible. To make $\bullet\bullet\text{--}\bullet\bullet$ and $\bullet\text{--}\bullet\bullet\bullet$ radiate enhanced lines will require a potential of $4\cdot75 + 7\cdot4 = 12\cdot1$, so that the electron stream—now over 25 volts—could make a small proportion radiate in this way, and we should expect a small enhanced radiation effect, gradually increasing as the volts rise from 25 to 73. This will be superposed on a

* Possibly the self-induction in the circuit kept the initial voltage above 4·7 volts just after the lowering.

strong atomic or He radiation. Thus, even before the 73·9 is reached, there will be a growing and noticeable radiation of enhanced quality, and the increase of this at 73·9 may not be sufficiently marked to show the rate of change of the total. In other words, the direct radiation point of 73·9 would be smoothed out. Somewhat similar effects would ensue also at the ionization point, except that the total change produced by direct ionization would be much greater and the change at 80 volts distinctly marked.

The existence of two kinds of prepared atoms suggests a possible radiation difference. For instance, on the orbit theory of levels, the orbits must differ with what we may call different cores, as distinct from nucleus—i.e., the "core" is the nucleus with internal electrons. Here there would be two kinds of cores, $\bullet\bullet\dots$ and $\bullet\dots\dots$. We are tempted to take the second set of radiations as those of the HeP' . Now the difference of the two limits in P' and P'' is

$$34853 (\text{He}'') - 32033 (\text{He}') = 6420,$$

which is equivalent to ·8 volt; and it is just this ·8 volt which Kannenstine's results as to the dying of the current in two steps suggest. With several stages in preparation, a larger number of these cores would be at disposal, and on this basis a larger number of sets might be expected in each spectral series type. Indeed, this seems to be actually the case in the other gases.

Neon *.

Rad. 11·8; 17·8.

Ion. 16·7; 20·0; 22·8.

4. In neon we find (1) a second set of radiation and ionization potentials, 11·8, 16·7, with the same difference as the 17·8, 22·8, which appears after the volts have been raised beyond 22·8 and then backed; and (2) the existence of a third ionization potential 20·0, none belonging to Ne^+ radiators. The Ne^+ have not been investigated. The first phenomenon was explained on the same basis of the existence of long-lived prepared atoms after a sufficiently high potential had been exerted, but there still remained the difficulty that as this new potential was greater than 13·5 ($n > N$), the radiation could not have been produced by a fully prepared atom. This, however, can be surmounted if more than one stage of preparation for gases beyond He exist—that is, for those possessing one or more sheath levels.

* Horton & Davies, Proc. Roy. Soc. *xviii*. p. 124 (1920).

The second set of potentials in Ne may then be supposed produced direct from configurations $\dots\bullet\dots\bullet$. It may be interesting to attempt to obtain on this basis an estimate of the preliminary and other voltages for Ne, starting from Horton and Davies's* observations on the entrance of different lines as the voltage is increased. They are given with their several Zeeman patterns in the 'Analysis' (p. 213). In A and the heavier gases the preponderating system of lines belong to the triplet type, analogous to those of group II. In this system the lines relating to the potentials are two, $s'-p'$ and $s'-p_2''$, corresponding therefore to the same ionization potential and two independent radiations. These series have Zeeman patterns respectively 0/1/1 and 0/3/2. Although in Ne these triplets either do not exist or are far down in the ultra-violet, we should expect corresponding singlet types to be related to the potentials, and we must look for strong lines corresponding to these types and having the above Zeeman patterns. Amongst those which Horton and Davies find as appearing at the lowest voltage are two lines with these patterns, viz. 5852 (s_21-p_22) and 6074 (s_41-p_22), the s, p referring to Paschen's allocations of types. But it must not be forgotten that there is evidence that the usual patterns exhibited by different series contain only the strongest components, some elements (*e.g.* Hg, Ba) showing additional ones. This would certainly be expected to be the case in Ne, which is notable for its complicated patterns. On this basis we should include also the lines

6402	s_5-p_6	0.1.2/6.7.8.9.10/6
6096	s_4-p_4	0.2/11.13.15/11,

which, omitting the components after the first, both reduce to 0/1/1, but no others reduce to 0/3/2. Now s_2, p_1, p_3, p_4 are subsidiary sequents, all link-connected, s_4, s_5 are the typical, and p_6 with p_8 the strongest of the p . Moreover, taking our assumption as to multiplicity of Zeeman pattern to be correct, the very numerous components in 6402 would seem to show that this is the representative of—at least—the chief $s'p'$ line. Provisionally we will take it so. Hence the limit is $s_5(1)=39887$; $p_62=24272$, so that the wave number of the line is 15615. These give for the true ionization potential 4.92 volts and true radiation 1.91. With the observed ionization of 22.8, this gives the first full preliminary potential = 17.9. Hence the observed radiation potential should be $17.9 + 1.91 = 19.8$, whilst actually it is

* Phil. Mag. xli. p. 921 (1921).

17·8, which means that the radiation begins from the prepared atom at once. But this is what we have learnt to expect from a long-lived prepared atom. There ought to be a large increase of radiation at 19·85, but any such effect might possibly be masked by the existence of the additional ionization potential at 20 volts. We should expect a radiation potential due to the $s'p_2'''$ line (Z.P.=0·3'2). If the representative of this line is the doubtful 6074, the potentials would not be distinguishable from the others.

The "backed" set 11·8, 16·7 are 6·1 below the other. In other words, 6·1 volts have previously been applied. Thus the work to change the stage $\dots\bullet-\bullet\dots$ to $\dots\bullet-\bullet-\bullet\dots$ is 6·1 volts, and to change the latter $\dots\bullet-\bullet-\bullet\dots$ to $\dots\bullet-\bullet-\bullet-\bullet\dots$ is $17\cdot9-6\cdot1=11\cdot8$. It may be just possible that the ionization potential of 20 may be that required to ionize the intermediate stage $\dots\bullet-\bullet-\bullet-\bullet\dots$.

An objection, which appears serious, may be raised to the choice of the lines taken as the potential representatives. In He, and as we shall see in A, the corresponding lines have each of their sequents (termed as Paschen calls them) both of order $m=1$, whereas the above-mentioned in Ne have one p_9 (indeed all the p limits), with $m=2$. We should certainly be surprised if Ne does not stand in line with the others. It might be explained by supposing that these $m=1$ lines exist, e. g., $p_9=N/(2\cdot12)^2$, so that the first order would be in the neighbourhood of $N/(1\cdot12)^2$ or 87600, with negative n as in A and radiation potential of magnitude about $(87600-39887)/8100=5\cdot9$. But this again is out of step with He and A.

Argon.

Rad. 11·5. Ion. 15·1.

5. In argon a very doubtful attempt was made to illustrate the theory of the preliminary and true potentials by identifying two ultra-violet lines by Lyman as the representatives of $s'-p'$ and $s'-p_2'''$. At the time the author was under the impression that this ultra-violet spectrum belonged to the red. Reference, however, to Lyman's paper shows that it belongs to the blue, and that the red spectrum definitely has no prolongation into this region. Moreover, as will be shown later, one of the lines involved belongs to the enhanced or A^+ system. In the present note an attempt is made to obtain a more secure basis by first determining the singlet and enhanced series on which the lines related

to the potentials depend. This discussion is given in § 6 below.

The potentials 11·5 and 15·1 are those determined by Horton and Davies *. As other observers had obtained values for the ionization varying between 15 and 17, they returned to the problem, and they † have lately published the results of an investigation in which they simultaneously observed current changes and the first appearance and the intensity changes in the spectrum as the accelerating potential was increased. The first part of their paper deals with voltages up to 20 in which atomic radiations only enter. They find :

- (1) the change in rate of increase of current at 11·5 is small ;
- (2) there is a more marked change at about 15 ;
- (3) at a few volts above 15, just over 17, there is a sudden sharp rise in current, and at this point the spectrum breaks out, showing lines belonging to the red spectrum.

They attribute this to increase of the electron stream due to neutralization of space electrification. One criticizes the conclusions of such experienced workers with some diffidence. But it is difficult to see how this space electrification can be neutralized without the entrance of + ions, which means the previous ionization of the gas. In other words, I would regard this new potential of 17+ as the real ionization, *i. e.* that at which an electron at one impact prepares the atom and ejects one of its electrons. It is the instant at which ionization is produced at one impact that the large effects are produced and the spectrum strongly appears. Space electrification is then diminished and the total electron stream is further increased, but it is a sequel and not a cause. With 17+*x* as the typical observed ionization, those originally observed at 11·5 and 15·1 would correspond to the analogous "backed set" in Ne, *i. e.* be due to direct impacts on atoms in one of the intermediate stages. The radiation from these less numerous centres would explain the slight increase of current observed at the 11·5 point. The preliminary potential would then be 17+*x*—true ionization, in which the true ionization is to be determined from spectral data which we must now consider.

The lines observed by Horton and Davies all belonged to

* Proc. Roy. Soc. xcvii. p. 23 (1920).

† *Loc. cit.* cii. p. 131 (1922).

the red spectrum, and could be arranged in two categories. In one the intensities increased on backing for a time before the final decrease to extinction. In others they decreased continuously. Amongst the first set they give 4510, 4345, 4272. These are A_5 , A_6 , C_3 of Rydberg's Type II.* It is probable, therefore, that all of the set belong to this type. They seem to have some analogy to the secondary spectrum of H and the so-called band spectrum of He. Of the other category, 7067, 6967 are given as appearing amongst the first and gradually increasing with the voltage. On our supposition as to the nature of the lines associated with the potentials, they should belong to singlet series $s'-p'$, $s'-p_2'''$ —of which, however, more than one set appear to be peculiar to the rare gases. The sets, however, are so near that the corresponding volt differences are inappreciable. The above two, for instance, only differ by .02 volt. The line 6967 shows the normal triplet 0/1/1 corresponding to $s'-p'$. We shall adopt then 6965 as the required $s'-p'$, and 7067 as $s'-p_2'''$. The Zeeman pattern for 7067 has not been investigated, but there is also support for this allocation of type in the fact that there is a weak line 7029 (intens. 1 compared with 7 for 7067) at a separation of 75.28 ahead. Now the triplet separation ν_3 or $p_3'''-p_2'''$ is 75.6, the same within observation errors. In other words, there is evidence of the presence of a line $s'-p_3'''$ if the wave number is negative. Any such line should be weak. We shall take this indication that the wave number is negative. Therefore, using I. A.,

$$\lambda = 7067.218 \uparrow,$$

$$s'-p_2''' = -14145.94.$$

Now, from the already known triplet series of A,

$$p_2''' = 51912.28, \text{ whence } s' = 37766.34.$$

If this allocation is correct, it should be accompanied by other lines of the series $s'(1)-p_2'''(m)$ in the red spectrum, and possibly of the combinations $p'''(1)-p'''(m)$, involving p_1, p_2, p_3 in the blue spectrum. Unfortunately the values of $p'''(m)$, $m > 1$, are not known directly, as the corresponding $P'''(m)$ lie in the ultra-violet far beyond any observed

* Query, are these Type II. really radiations from our supposed intermediate stages?

† Meissner, *Ann. d. Phys.* li. p. 115 (1916).

region. But a search shows that the series and combinations exist (see § 6 below). There is therefore converging and ample evidence that $\lambda=7067$ is the representative for $s'-p_2'''(m)$, and that consequently $s'=37766\cdot34$.

Passing now to $\lambda=6965\cdot432^*$, $n=14352\cdot62$, we must put

$$\begin{aligned}s'-p' &= \pm 14352\cdot62, \\ p' &= 37766\cdot34 \mp 14352\cdot62.\end{aligned}$$

If 6965 is the representative of the first order of the series, as its great intensity indicates, p' corresponding to $m=1$ must be large, or the lower sign must be taken. This is supported also by the fact that a weak line 6870 exists which is separated from 6965 by the same amount, $206\cdot7$, as 6965 is from 7067. This exact agreement shows that $206\cdot7$ is a real relation, and consequently

$$s'-p'-(s'-p''')=p'''-p'=\pm 206\cdot7 \text{ or } s'-p' \text{ and } s'-p'''$$

are of the same sign. Hence

$$p'=52118\cdot96.$$

Again, if this allocation is correct, other lines belonging to the series $s'-p'(m)$ should be found. This is so and also other lines corresponding to $p'-s'(m)$, combinations $s'(1)-s'(m)$, and indications of collaterals of $p'(1)-p'(m)$. For our present purposes we need only the first lines now considered fully established :

$$\begin{aligned}s'-p_2''' &= -14145\cdot94, & s'-p' &= -14352\cdot65 \\ \text{with } s' &= 37766\cdot34, & p' &= 52118\cdot96.\end{aligned}$$

But at present there is nothing to show whether those named s' , p' should not be the typical p' , s' . This would seem to be settled by the fact that the series $s'-p_2'''m$ is found, and not $p'-p_2'''m$. In other words, $s'=37760\cdot34$ is the limit which settles the ionization potential. There results

$$\text{true ion. potential} = 377\cdot6681/81 = 4\cdot66.$$

$$\text{rad. potentials} = 143\cdot526/81 = 1\cdot772,$$

$$= 141\cdot459/81 = 1\cdot746,$$

whence the first preliminary potential

$$= 17 + x - 4\cdot66 = 12\cdot3 + x.$$

* Meissner, *Ann. d. Phys.* li. p. 115 (1916).

With our long-lived prepared atoms we should expect radiation to begin at this voltage, but any such radiation point would be smoothed out, in the way explained in the Ne discussion, by the presence of the radiation caused by direct impacts on the intermediate stage, and showing itself at 11.5.

The continuance of the spectrum on backing is explained as in He and Ne. With very intense electron streams the voltage could be reduced below 11.5 without the lines disappearing. The lowest value to which it could be backed was 6.5 volts. This denotes the value at which the lines ceased to be visible, so that the real limiting value would probably be slightly less. The theoretical limiting backing point is the "true" ionization potential or 4.7.

It is very desirable that Kannenstine's experiments should be extended to Ne, A, and the other gases. Our results show that it is probable that with sufficiently high frequencies, the arc would strike in A at 4.66 volts, and that it would die away in more than two steps.

We now pass to the consideration of the enhanced or A^+ potentials. There is no justification for the assumption sometimes made that the blue (or spark) spectrum is due wholly to ionized atoms. The blue spectrum comprises, with enhanced lines, also the typical triplet series, which always require a higher voltage to produce their lines than do their associated singlet systems. The latter, as we have seen, predominate in the red spectrum, which contains in addition the Type II. spectrum. With increasing voltage the lines of the triplet series in the blue spectrum should begin to appear, even before the second ionization is reached. The reason why Horton and Davies have not observed them is that none exist in the visible region in which their observations were made. The nearest is $D'''(1)$, $\lambda 4203$, or perhaps $F'''(3)$, about $\lambda 4980$, both outside. The first appearing should be $P'''(1)$, $\lambda 2344$, and afterwards $S'''(2)$, $\lambda 3765$. In the case of A^+ the line on which the potentials depend is the chief doublet line P_1'' .

In extending their investigations they found that as the voltage further increased, the blue lines appeared at about 19 volts. "Their intensities increased as the voltage was raised from 19 to about 24 volts, after which it did not increase further until the voltage reached 34. From 34 volts up to 42 volts the blue spectrum lines increased very much in intensity." The increase in intensity was first noticeable

at 34 volts. Their tables * I., II., III. give a view of the appearance and change of intensities of these lines as the potential increased in steps of 2 volts from 19 to 42. The great increase after 34 is apparent at a glance. The lines they specially note as first appearing are $\lambda\lambda 4430\cdot4$ and $4426\cdot2$, whilst the table shows 4348 as quite distinctly the first to appear, and the first to intensify. The sudden rise in intensity at 34 (especially in 4348) is a clear indication that atoms are now being doubly ionized at one electron impact. The entrance of the lines at 19 shows either that the real radiation potential has been reached, or that some of the numerous prepared atoms present are being made to radiate. Their fig. 5 would seem to show that the ionization potential must be close to $34\cdot0$. But it must not be forgotten that the gas contains now a very large proportion of prepared atoms, and that 34 volts may refer to their ionization, and that the normal atom might require a higher voltage.

For further progress it is necessary to know the enhanced doublet series in this element, which have not yet been allocated. An attempt to do so is made in § 6 below. For reasons there given, I do not feel complete certainty in the correctness of the allocation, although the three arrangements for S'' , P'' , D'' hold well together. A complete test is difficult because the higher orders run down into the far ultra-violet, and especially because a knowledge of the Zeeman patterns for the lines in question is wanting. The result is that the first-order P'' lines are (Kayser's measures) :

	$\lambda(\text{R.A.})$.	I.	n .	
$P_2(2)$	4426.165	8	22586.70	
$P_1(2)$	4348.222	9	22991.57	404.87

with the limit $P_1(\infty) = 80965$.

With these allocations we find

$$\text{true rad. pot.} = 222.91/81 = 2.84,$$

$$\text{true ion. pot.} = 809.65/81 = 9.25.$$

With the observed ionization at 34, the preliminary potential, *i. e.* that required to eject one electron and raise

* For our purposes these tables should be regarded as one. Stark's categories indeed almost certainly comprise lines emitted by related configurations, but any definite interpretation of their state of ionization involves many difficulties ('Analysis of Spectra,' p. 111). It is generally understood that Stark himself has now somewhat modified his views.

the other to the radiating stage, is $34.0 - 9.25 = 24.8$. All this is on the assumption that 34 volts is that required to fully ionize the normal atom $\dots \bullet - \bullet \dots$. As it takes $17 + x$ volts to produce A^+ , it leaves $7.8 - x$ as the work required to raise the second electron to the radiating state after the first has been ejected: in other words, less than to raise the first when the second is present. We should expect it, as in He, to be more than double. This is an indication that the 34 volts potential does not refer to ionization of the normal atom at one electron impact, but to ionization of the atom at an intermediate stage. The real ionization of the atom to A^{++} must be at a few volts above $17 + 2 \times 17$, or greater than 51. It is, of course, possible that before this potential has been reached the greater proportion of the normal atoms may have been transformed into intermediate stages, especially that represented by the fully prepared atom $\bullet \dots \bullet$, in which case no increase of ionization would be apparent at this highest voltage. We should scarcely expect a long life for the A^+ atom, either $\bullet \bullet \dots$ or $\bullet \dots \bullet$, so that the proportion present would not be large except for intense electron streams. It would account, however, for the first faint appearance of enhanced radiation at a little over 19 volts. With several possible stages it is impossible to say in detail what would happen without a knowledge of their various lives. But it may be suggested that the 34 volts may be due to the ionization of $\bullet \bullet \dots$ produced by preparatory + ion. pot., supposing the preparatory voltage for the second preparation after the first electron is ejected is somewhat larger than twice the first preliminary. If this be $2(12.3 + x)$, we should require

$$24.6 + 2x + 9.25 = 34,$$

$$x = .07.$$

Nothing is to be gained at present by attempting a more intimate analysis.

The singlets and doublets of argon.

6. The triplet separations in A are $\nu_1 = 179.50$ and $\nu_2 = 75.60$. The limit of the S_1 series, as determined from the first three lines, is 51731.05 R/A, whence $S_2(\infty)$ or $p_2'''(1)$ is 51912.28 I/A. The first and third orders lie in the ultra-violet with considerable possible observation errors, so that 51912 is subject to an uncertainty of a few units. In fact,

the value * as deduced from the difference and summation series **F** and **F**, give it about 2 larger.

The problem of determining the singlet series is complicated by the suspicion that these gases possess several sets of each type and by the certainty that displacement is very prevalent. Many of the red lines appear disrupted into several collaterals in the blue. Also these singlets in general do not appear very amenable to the usual formulæ. We have the direct evidence, however, indicated above, for the $P'(1)$ and $s'1-p_2'''1$, and thus get secure starting-points. The lines given in the following tables for S' , P' appear to form at least one set of related series. The $O-C$ are not large compared with the possible, and are considerably diminished if the limits are taken a few units larger, as indicated above. But there are peculiarities. Whilst the combination $p'1-p'2$ is not a good agreement (displacement 10), there is a very close one for a sort of satellite to $p'(1)$, $n=14410\cdot4$, and the same line serves as the first of a $p'1-\sigma'm$ set which form combinations with the s' . In general, in the successive orders of the $p'''m$, the values of the Δ are very nearly the same or between Δ and $\cdot8\Delta$. It is thus easy to obtain approximate estimates of the values of the p''' separations for different orders although the lines themselves are not known. Here $\Delta_1=2519$, $\Delta_2=1057$, and the resulting ν_1, ν_2 for $m=2, 3$ with the same Δ are

$m=2$	$\nu_1=37\cdot37$	$\nu_2=15\cdot70$
$m=3$	$\nu_1=13\cdot40$	$\nu_2=5\cdot63$

and may be somewhat less. It will be seen that these appear in the combinations $p'''1-p'''m$. These series deserve a more exhaustive investigation in connexion with a comparative study of the same series in the heavier gases. But it is too large a question for the present note. The important point here is the support they give to the allocation of the first lines $P'(1)$ and $s'1-p_2'''1$.

In the enhanced doublet series, the P, S, D series, with $\nu=404\cdot63$ appear to hang well together, with formulæ of normal types, as well as representatives of the $p''2-p'''3$ combinations. There is evidence of a large number of related sets shown by the large number of the 404 separations in the spectrum. The normal ν separation for this type has a value a little larger than twice the triplet ν_1 —here 360—for which 404, although rather large, may serve. But perhaps the more significant relation is that in enhanced series in group II the mantissæ difference on which ν depends is always about

* Trans. Roy. Soc. ccxx. p. 446.

the same as the triplet $\Delta_1 + \Delta_2$, here 3576. But with the limit here used, $S_1(\infty) = 63973$, the difference required is 8243, of the order of 1438, far exceeding the value of the own multiple known for any other case. The 3576 would produce a separation of about 18). I suspect, therefore, that the actual limit of the true series is much larger, with this $3576 + ?$ producing $\nu = 404$. In that case the series here adopted would be linked to normal ones †, and the formula for ρm would be different. Further, many of the lines are attached to others by triplet links, of the possibility of which between enhanced and triplet series we have no experience. The matter must be left for further discussion before complete certitude of the correctness of the allocations can be felt.

In the tables, measures in R.A. are printed in italics. Small brackets after numbers or below the tables refer to the references immediately following this. Numbers enclosed in square brackets are calculated values. r, b refer to the red and blue spectra respectively.

References.

1. H. KAYSER.—*Astro. J.* iv. p. 1 (1896).
2. J. M. EDER and E. VALENTA.—*Denks. Wien. Akad.* lxiv. p. 216 (1896).
3. T. LYMAN.—Spectroscopy of extreme ultra-violet.
4. K. W. MEISSNER.—*Ann. d. Phys.* li. p. 115 (1916).
5. C. RUNGE and F. PASCHEN.—*Astro. J.* viii. p. 97 (1898).

TABLE I.

m .	$\left. \begin{matrix} P' \\ \sigma'(1) - p'm \end{matrix} \right\}$				$\left. \begin{matrix} S' \\ p'1 - \sigma'(m) \end{matrix} \right\}$			
	I.	λ .	n .	$d\lambda$.	I.	λ .	n .	$d\lambda$.
1	8	6965.432 ¹ r	14352.65	*	8	6965.432 r	14352.65	*
	1	6937.8 r	14410.4		1	6937.8 r	14410.4	
2	5	5188.46 ¹ r	19268.91	*	4	2692.8 b	37126.6	*
					8	2708.40 b	36912.64	
3	2	3514.513 r	28446.43	-3	3	2255.2 b	44134.2	-27
					2	2253.0 b	44177.1	
4	...	...	[32133.80]		1	2120.0 b	47156.7	-3
5					1	2059.5 b	48751.8	-23

1 a (4); 1 b , 2, 3 (1).

1 a (4); 2...5 (2); 1 b (1).

¹ Zeeman Patterns, 0/1/1.

† Such parallel sets are the rule in the triplet systems of Kr, X.

Combinations.

 No $s'-s''m$, but

$s'1-s'2$	3	4431.172 (1) <i>b</i>	22561.93 [... 60.0]
$s'1-s'3$	2	3352.248 (1) <i>b</i>	29823.32 [... 24.68]
$s'1-s'2$	5	4401.156 (1) <i>b</i>	22715.81 [... 16.2]
$s'1-s'3?$	1	3361.973 (1) <i>b</i>	29737.05? [... 23.9]+13
$s'1-s'4$	3	3054.846 (1) <i>b</i>	32726.64 [... 24.0]
$p'1-p'2?$	1	2972.60 (1) <i>r</i>	33632.07? [... 621.66]+11
$p'1-p'3$	beyond obs. in red.		
$w'1-p'2$	2	2968.39 (1) <i>r</i>	33679.78 [... 9.27]

all measures by (1).

$$P' = 37766.34 - N/\{m + 419427 + 031228/m\}^2,$$

$$S' = 52118.99 - N/\{m + 705374 - 001260/m\}^2.$$

TABLE II.

$s'1-p_2'''m.$					$s'-w_2'''m.$		
<i>m.</i>	I.	$\lambda.$	<i>n.</i>	$d\lambda.$	I.	$\lambda.$	<i>n.</i>
1	7	7066.218 <i>r</i>	-14145.94	*			
	1	7029.21 <i>r</i>	-14223.0				
2	2	5010.42 <i>r</i>	19953.7	*	4	4965.239 <i>b</i>	20135.17
3	2	3476.894 <i>r</i>	28754.52	1.46 ³	2	3464.564 <i>b</i>	28858.18
4	...	...	[32338.82]				

 1 *a* (4); 1 *a*, 2, 3 (1).

2, 3 (1).

¹ is $s'1-p_3'''1$.

² This line is omitted by Kayser in his Handbuch. The value as given in the blue spectrum is 5009.426, $n=19957.57$. It agrees better with the combinations below.

³ or the line is $s'-p_1'''(3)$.

 Combinations (the $'''$ are omitted).

p_21-p_22	3	2931.52 (1)	34103.36	79.74 [... 3.51]
p_31-p_22	4	2924.68 (1)	34183.10	
p_21-p_23		not obs.	[42911.32]	14.2
p_21-p_13	3	2339.9 (2)	42725.51	[... 24.72]
p_21-p_24	2	2151.2 (2)	46472.7	[... 84.76]
p_11-p_14	1	2159.3 (2)	46298.5	[... 310.7] 174.0

 The obs. $m=4$ are 12 behind the calculated.

p_11-w2	3	2931.52 (1)	34103.4	179.6 [... 81.1]
p_21-w2	2	2916.3 (2)	34283.0	[... 4.12]
p_21-w3	1	2324.7 (2)	43004.4	

$$p_2'''(m) = N/\{m + 509272 - 055732/m\}^2.$$

S".

TABLE III.

D".

m.	I.	λ .	n.	$d\lambda$.	m.	I.	λ .	n.	$d\lambda$.
2	9	4348.222	-22991.57	*	2	3	6644.2	-15046.64	
	8	4426.165	-22586.70			3	6699.06	-14923.41	*
3	5	4430.355	22565.34	*	3	1	6827.83	-14641.98	*
	4	4352.368	22969.67			7	...	[24850.3]	
4	3	2512.3	39792.4	*	3	3	4014.002	24005.89	*
	1	2487.0	40197.1			3	3958.529	25254.91	*
5	1	2077.2	48126.6	13	4	1	...	[40733.71]	
			[48531.30]			2	2453.0	40754.3	
6	...	...	[52792.47]	5	...	...	...	41138.4	
								[48603.83]	
								[48614.8]	
								[49008.4]	

2, 3 (1); 4, 5 (2).

2a, 3 (1); 2b, c (5); 4 (2).

 $v=404.63$.

$$S_1(m) = 63973.65 - 4N/\{m + 272739 - 053466/m\}^2,$$

$$D_{11}(m) = 63973.65 - 4N/\{m + 336896 + 042312/m\}^2,$$

$$D_{12}(m) = 63973.65 - 4N/\{m + 333436 + 045552/m\}^2.$$

TABLE IV.

P".

m.	I.	λ .	n.	v.
2	8	4426.165	22586.70	404.87
	9	4348.222	22991.57	
3	9	1855.7	53870.3	160.4 ¹
	4	1850.2	54030.7	
4	...	...	[66808.5]	
			[60728.9]	

2 (1); 3 (3).

¹ Abnormal separation, should be 150 or less, and intensities abnormal.

Combinations.

$p_1 2 - p_2 3$	2	3237.920 (1)	30875.30	150.8	[... 78.7]
$p_1 2 - p_1 3$	1	3222.183 (1)	31026.10	418.46	[39.1]
$p_2 2 - p_1 3$	1	3179.30 (2)	31444.56	148.6	[43.7]
$p_2 2 - p_2 3$	3	3194.440 (1)	31295.93		[83.6]

The normal separation for $m=3$ is 147 or less. That for $m=3$ of 160 is excessive and is due to displacement. The combinations show the normal values. These combinations show that the displacement is in $p_1(3)$ causing a shift of 13, say $p_1(3)(x\delta)$, x about 12. Then in the second combination $p_1 3$ is normal, in the third it is $p_1(3)(x\delta)$, and in the fourth the same displacement is continued in p_2 and is $p_2(3)(x\delta)$. This displacement in $p_1(3)$ will affect the constants in the formula for $P_1(m)$:

$$P_1(m) = 86965.22 - 4N/\{m + 711777 - 186144/m\}^2,$$

$$P_2(m) = 86965.22 - 4N/\{m + 701675 - 182466/m\}^2.$$

December 8, 1922.

LIII. *Thermodynamics and Statistical Mechanics.* By
R. H. FOWLER, M.A., *Fellow and Lecturer in Trinity
College, Cambridge* *.

§ 1. *INTRODUCTION and Summary.*—In a series of papers † a method has been developed for calculating the distribution laws for assemblies in statistical equilibrium. The more general case is treated in the third paper, which deals with assemblies in which dissociation can take place. All the results obtained are proved purely as theorems in statistical mechanics based on the general principles of the quantum theory, and include the laws of dissociation-equilibria in perfect gases and of the vapour-pressure of crystals. No appeal is made at any stage to thermodynamic arguments—a feature which may legitimately be claimed as an advantage in molecular statistics.

The equilibrium conditions of statistical mechanics are in general independent of the molecular mechanisms by which exchanges of energy are effected. It is not until the study of reaction velocities and analogous problems is taken up that the molecular mechanisms themselves become really of first-class importance. In spite of this limitation, the theory of statistical equilibrium does take one a definite step beyond the field of classical thermodynamics, and for the systems to which it is applicable it must imply thermodynamical laws. It is therefore of some interest and importance to deduce the laws of thermodynamics from the theory of statistical equilibrium with the widest possible generality. This is especially the case for the third law—i. e., Nernst's Heat Theorem,—as Ehrenfest and Trkal ‡ point out in a very interesting paper on this subject which is quoted extensively in the third paper. We have already done this for certain assemblies in which the number of individual systems of every type is fixed §. It is now possible to extend the argument to assemblies in dissociative equilibrium.

* Communicated by the Author.

† Darwin and Fowler, *Phil. Mag.* xliv. pp. 450, 823 (1922); Fowler, *Phil. Mag.* xlv. p. 1. These will be cited as first, second, and third papers respectively.

I take this opportunity of expressing my indebtedness to Mr. Darwin, whose share in the work is really by no means confined to the two papers written in collaboration. Mr. Darwin, however, must not be held responsible for any erroneous statements which may be found here.

‡ Ehrenfest and Trkal, *Proc. Sect. Sciences Amsterdam*, vol. xxiii. p. 162 (1920).

§ Darwin and Fowler, Second paper.

Phil. Mag. Ser. 6. Vol. 45. No. 267. March 1923. 2 K

The paper just referred to starts with a critical examination of the usual presentation of entropy in statistical mechanics. We were forced to conclude that a proper logical account of entropy starting from the well-known hypothesis of Boltzmann is, if possible at all, necessarily somewhat recondite, and that the most satisfactory method is to use the classical equation $dQ = TdS$ in the classical way. The idea of entropy in statistical mechanics seems, in fact, to be of secondary importance, and can usually, if not always, be dispensed with altogether. It is unnecessary to repeat this discussion, which applies with at least equal force to the dissociating assemblies considered here. We shall accept the results and define the entropy of a dissociating assembly in the first instance by the classical equation.

The contents of this paper are briefly as follows:—After summarizing in § 2 such of our previous results as are relevant, we prove in § 3 that for dissociating assemblies in statistical equilibrium it is possible to define functions S and T which satisfy the equation $dQ = TdS$ and have all the properties essential to entropy and absolute temperature in thermodynamics. Incidentally we thus establish in the only completely logical way the relation between the empirical temperature θ and the absolute temperature T for such assemblies*. We obtain expressions for the entropy of the various groups of systems in the assembly which depend in a definite way on the number of systems in any group. In § 4 we show how the connexion with thermodynamics can alternatively be made by means of Planck's Characteristic Function. Up to this point we have assumed the point of view to which we were led by the discussion of the second paper. In § 5 we reopen parts of this discussion and examine shortly possible definitions of entropy for dissociating assemblies in connexion with the increasing property. This property is deduced in § 6 for entropy, suitably defined, from the characteristics of statistical equilibrium.

We have thus shown that there exists for the assemblies with which we deal a function of their state, the entropy, with all the requisite thermodynamic properties. The laws of Thermodynamics and their consequences are therefore

* We have insisted that the ideas of thermodynamics are of secondary importance in statistical mechanics. Here, in the logical introduction of T , they are, however, necessary; this is natural, for the *absolute* temperature scale is essentially a thermodynamic idea.

true for such assemblies. We show further, in § 7, that Nernst's Heat Theorem must also be true for them. It is a direct consequence of the characteristics of statistical equilibrium, on one condition—that the weights of the lowest quantum states of the reacting systems are equal. There is every theoretical reason to suppose that this condition is fulfilled by all condensed systems, or at any rate by all crystals. In this way, this theorem and the resulting properties of the chemical constants can be placed in their true perspective as theorems in statistical mechanics. It is not necessary to postulate the existence of entropy at any stage in the argument.

The general object of the paper is to amplify the discussion of our second paper with the help of the additional theoretical material now available.

§ 2. *Summary of previous results.*—The essential features of our method—the calculation of *average* values, the idea of weight, the use of partition functions (Planck's "Zustandsumme" in another form), and the complex integral for the total number of weighted complexions representing the assembly—are expounded in the first two papers and fully summarized in the third. They must be taken for granted here without further introduction. We must recall, however, the notation and formulæ. It will be sufficient to give these in their general form applicable to cases of dissociation.

Consider an assembly with $M_1 \dots M$ free atoms and $N_1, \dots, N_j$ free molecules. Let $g_1(z), \dots, g_s(z), h_1(z), \dots, h_j(z)$ respectively be their partition functions for the kinetic energy of translation and potential energy in any external fields of force. Let $b_1(z), \dots, b_j(z)$ be the partition functions for the rotational and vibrational energy (internal) of the molecules. The potential energy depends on certain parameters $y_1, y_2, \dots$ defining the external fields of force. The walls of the enclosure containing the assembly can be regarded as the limit of intense local fields of force, and are thus included above. We can only consider the case in which each type of gas is perfect, and then

$$g(z), h(z) = \frac{(2\pi m)^{3/2} V}{h^3 (\log 1/z)^{3/2}}, \quad \dots \quad (2.1)$$

where m is the mass of, and V the volume* of the container

* The volume can be different for the different atoms and molecules if some of the walls are semi-permeable.

available to the atom or molecule concerned. Let E be the energy of the assembly, supposed zero when all the molecules are dissociated and the resulting atoms all at rest in a field of potential zero. E so defined can be negative, but that is of no account. Let $\chi_1, \chi_2, \dots$ be the energies required to dissociate the respective molecules, at rest in their lowest quantum state, into their individual atoms at rest. Then the number of weighted complexions c of any one example of such an assembly is

$$c = \frac{1}{2\pi i} \int_{\gamma} \frac{dz}{z^{E+1}} [g_1(z)]^{M_1} \dots [g_s(z)]^{M_s} \left[\frac{h_1(z)b_1(z)}{z^{\chi_1}} \right]^{N_1} \dots \times \left[\frac{h_j(z)b_j(z)}{z^{\chi_j}} \right]^{N_j}. \quad (2.2)$$

The integral is taken round a contour γ , which is any circle with its centre at $z=0$ and radius less than unity. The number of different examples of such an assembly with the same M 's and N 's is *

$$\frac{X_1! \dots X_s!}{M_1! \dots M_s! N_1! \dots N_j! \sigma_1^{N_1} \dots \sigma_j^{N_j}}, \quad (2.21)$$

where $X_1, \dots, X_s$ are the total number of atoms of each type (including those in the molecules) and $\sigma_1, \dots, \sigma_j$ are the symmetry numbers of the molecules. The number of weighted complexions representing a specified statistical state of the assembly in which there are $M_1, \dots, M_s$ atoms and $N_1, \dots, N_j$ molecules of each type is therefore

$$\frac{X_1! \dots X_s! c}{M_1! \dots M_s! N_1! \dots N_j! \sigma_1^{N_1} \dots \sigma_j^{N_j}}. \quad (2.22)$$

If the r th molecule contains $q_{1r} \dots q_{sr}$ atoms of the various types, then

$$X_t = M_t + \sum_r q_{tr} N_r, \quad (t=1, \dots, s), \quad (2.23)$$

and the total number of weighted complexions for the assembly in any state (with given energy E) can be put in the form

$$C = \frac{1}{2\pi i} \int \frac{dz}{z^{E+1}} [g_1(z)]^{X_1} \dots [g_s(z)]^{X_s} \times \sum_{(N)} \frac{X_1! \dots X_s! \beta_1^{N_1} \dots \beta_j^{N_j}}{M_1! \dots M_s! N_1! \dots N_j!}, \quad (2.24)$$

* Ehrenfest and Trkal, *loc. cit.* p. 169.

where

$$\beta_r = \frac{h_r(z) b_r(z)}{\sigma_r^{2\chi_r} \{g_1(z)\}^{q_{1r}} \dots \{g_s(z)\}^{q_{sr}}}, \quad (r=1, \dots, j). \quad (2.25)$$

The summation $\Sigma_{(N)}$ is taken over all possible values of the N 's from zero (included) to the largest values which leave all the M 's positive or zero.

The conditions of statistical equilibrium follow at once. We find that $C\bar{N}_r$ is given by an integral identical with (2.24), except for the addition of a factor N_r under the summation sign $\Sigma_{(N)}$. After evaluation, we find that the equilibrium values $\bar{M}_1, \dots, \bar{M}_s, \bar{N}_1, \dots, \bar{N}_j$ are determined uniquely by the equations

$$\frac{\bar{N}_r}{(\bar{M}_1)^{q_{1r}} \dots (\bar{M}_s)^{q_{sr}}} = \beta_r(\vartheta), \quad (r=1, \dots, j), \quad (2.3)$$

combined with (2.23), provided that ϑ is determined as the unique root of the equation

$$E = \Sigma_t X_t \vartheta \frac{\partial}{\partial \vartheta} \log g_t(\vartheta) + \Sigma_r \bar{N}_r \vartheta \frac{\partial}{\partial \vartheta} \log \beta_r(\vartheta), \quad (2.4)$$

$$= \Sigma_t \bar{M}_t \vartheta \frac{\partial}{\partial \vartheta} \log g_t(\vartheta) + \Sigma_r \bar{N}_r \vartheta \frac{\partial}{\partial \vartheta} \log \{h_r(\vartheta) b_r(\vartheta)\} \\ - \Sigma_r \bar{N}_r \chi_r. \quad (2.41)$$

The quantity ϑ may be identified with the empirical temperature.

The foregoing equations still hold good if the assembly contains other systems which can share its energy besides the dissociating and associating free atoms and molecules. The only difference then is that the partition function for the additional systems appears as a factor in the integrand of (2.2) and of (2.24) outside the summation sign, and gives rise to an extra term in (2.4) and (2.41). We can in this way, for example, include the energy of the temperature radiation in the assembly. The results as functions of ϑ are unaffected.

Similar arguments apply to a crystal in equilibrium with its own vapour, if we may suppose that the partition function for the crystal of M molecules can be put in the form $[K(z)]^M$. If χ is now the work required to

* That this form is possible follows from Born's work. See Darwin and Fowler, Proc. Camb. Phil. Soc. vol. xxi. p. 262.

remove one molecule from the crystal in its lowest quantum state, and leave it at rest as a free molecule in its lowest quantum state, then the number of weighted complexions representing one example of such an assembly is

$$c = \frac{1}{2\pi i} \int_{\gamma} \frac{dz}{z^{E+1}} [K(z)]^M [b(z) h(z) z^X]^N \dots \quad (2.5)$$

The number * of examples of the assembly is

$$\frac{X_1! \dots X_s!}{N! \sigma^N} \dots \dots \dots (2.51)$$

If the total number of molecules is $X (=M+N)$, then the total number of complexions representing the assembly (X large) is proportional to

$$C = \frac{1}{2\pi i} \int_{\gamma} \frac{dz}{z^{E+1}} [K(z)]^X \exp \left\{ \frac{b(z) h(z) z^X}{\sigma K(z)} \right\}, \quad (2.52)$$

and

$$\bar{N} = \frac{b(\vartheta) h(\vartheta) \vartheta^X}{\sigma K(\vartheta)}, \quad \dots \dots \dots (2.53)$$

provided ϑ is determined by the equation

$$E = X\vartheta \frac{\partial}{\partial \vartheta} \log K(\vartheta) + \vartheta \frac{\partial \bar{N}}{\partial \vartheta} \dots \dots (2.54)$$

The distribution laws for either of these assemblies can be shown to be the same as if the values of the M 's and N 's were permanently fixed at their equilibrium values. The generalized force component† Y_1 tending to increase the coordinate y_1 of the bodies (walls) external to the system is

$$Y_1 = \frac{1}{\log 1/\vartheta} \left\{ \sum_t M_t \frac{\partial}{\partial y_1} \log g_t + \sum_r \bar{N}_r \frac{\partial}{\partial y_1} \log (h_r b_r) \right\}. \quad (2.6)$$

§ 3. *The entropy of an assembly in dissociative equilibrium.*—We shall show in this section that the assemblies of § 2 obey the laws of classical thermodynamics by showing that functions S and T exist satisfying the equation $dQ = TdS$.

* The number may differ from this by a constant factor which is irrelevant here. The X 's are the total numbers of atoms composing the molecules. We must think of dissociation exchanges as still theoretically possible, in order to extend fully the trajectory of the assembly.

† Second paper, § 7.

We take first the assembly of dissociating perfect gases. By the definition of dQ we have for any assembly,

$$dQ = dE + \Sigma Y dy.$$

Formula (2.6) can be written in the form

$$Y_1 = \frac{1}{\log 1/\mathfrak{s}} \left\{ \Sigma_t X_t \frac{\partial}{\partial y_1} \log g_t + \Sigma_r N_r \frac{\partial}{\partial y_1} \log \beta_r \right\}. \quad (3.1)$$

The reduction to (3.1) follows at once from the fact that σ and $\mathfrak{s}^x$ are necessarily independent of the y 's. Further, by (2.4), dE can be written in the form

$$\begin{aligned} dE = & \left[\Sigma_t X_t \left\{ \frac{\partial}{\partial \mathfrak{s}} \log g_t + \mathfrak{s} \frac{\partial^2}{\partial \mathfrak{s}^2} \log g_t \right\} \right. \\ & \left. + \Sigma_r \bar{N}_r \left\{ \frac{\partial}{\partial \mathfrak{s}} \log \beta_r + \mathfrak{s} \frac{\partial^2}{\partial \mathfrak{s}^2} \log \beta_r \right\} \right] d\mathfrak{s} \\ & + \left[\Sigma_t X_t \mathfrak{s} \frac{\partial^2}{\partial \mathfrak{s} \partial y_1} \log g_t + \Sigma_r N_r \mathfrak{s} \frac{\partial^2}{\partial \mathfrak{s} \partial y_1} \log \beta_r \right] dy_1 + \dots \\ & + \Sigma_r \left[\mathfrak{s} \frac{\partial}{\partial \mathfrak{s}} \log \beta_r \right] d\bar{N}_r. \end{aligned}$$

Then

$$\begin{aligned} dQ = & \frac{1}{\log 1/\mathfrak{s}} \left[\Sigma_t X_t d \left\{ \log g_t + \log 1/\mathfrak{s} \cdot \mathfrak{s} \frac{\partial}{\partial \mathfrak{s}} \log g_t \right\} \right. \\ & + \Sigma_r \bar{N}_r d \left\{ \log \beta_r + \log 1/\mathfrak{s} \cdot \mathfrak{s} \frac{\partial}{\partial \mathfrak{s}} \log \beta_r \right\} \\ & \left. + \Sigma_r \left(\log 1/\mathfrak{s} \cdot \mathfrak{s} \frac{\partial}{\partial \mathfrak{s}} \log \beta_r \right) d\bar{N}_r \right], \\ = & \frac{1}{\log 1/\mathfrak{s}} \left[d \Sigma_t X_t \left(\log g_t + \log 1/\mathfrak{s} \cdot \mathfrak{s} \frac{\partial}{\partial \mathfrak{s}} \log g_t \right) \right. \\ & \left. + d \Sigma_r \bar{N}_r \left(\log \beta_r + \log 1/\mathfrak{s} \cdot \mathfrak{s} \frac{\partial}{\partial \mathfrak{s}} \log \beta_r \right) - \Sigma_r \log \beta_r d\bar{N}_r \right]. \end{aligned}$$

But by (2.3)

$$\log \beta_r = \log \bar{N}_r - \Sigma_t q_{tr} \log \bar{M}_t.$$

Therefore

$$\begin{aligned} \Sigma_r \log \beta_r d\bar{N}_r &= \Sigma_r \log \bar{N}_r d\bar{N}_r - \Sigma_t \log \bar{M}_t (\Sigma_r q_{tr} d\bar{N}_r), \\ &= \Sigma_r \log \bar{N}_r d\bar{N}_r + \Sigma_t \log \bar{M}_t d\bar{M}_t, \end{aligned}$$

with the help of (2.23). Thus this term is also a perfect

differential, and $(\log 1/\mathfrak{S})dQ$ is a perfect differential. There exists, therefore, a function S of the equilibrium state of the assembly, called the entropy, and a function T of $\mathfrak{S}$ called the absolute temperature, which are such that $dQ = TdS$ if

$$\log 1/\mathfrak{S} = 1/kT, \quad . \quad . \quad . \quad . \quad (3.2)$$

$$\begin{aligned} (S - S_0)/k &= \sum_t X_t \left(\log g_t + \log 1/\mathfrak{S} \cdot \mathfrak{S} \frac{\partial}{\partial \mathfrak{S}} \log g_t \right) \\ &+ \sum_r N_r \left(\log \beta_r + \log 1/\mathfrak{S} \cdot \mathfrak{S} \frac{\partial}{\partial \mathfrak{S}} \log \beta_r \right) \\ &- \sum_r (\bar{N}_r \log \bar{N}_r - N_r) - \sum_t (M_t \log \bar{M}_t - \bar{M}_t). \quad (3.3) \end{aligned}$$

The integration constant S_0 must be independent of any parameter in (3.2) which can change in the assembly. That is, S_0 is independent of $\mathfrak{S}$, N_r , M_t , y_1 , y_2 , ..., but it can depend in any manner on the X 's. Except for S_0 and the proportionality factor k , S and T are thus uniquely determined, and the identification of $\mathfrak{S}$ and $e^{-1/kT}$ is made with the full generality which is only possible by such an appeal to the *form* of the second law of Thermodynamics.

We can put (3.3) into a slightly different form by eliminating the X 's with the help of (2.23). It then becomes

$$\begin{aligned} (S - S_0)/k &= \sum_t M_t \left(\log \frac{g_t}{M_t} + 1 + \log 1/\mathfrak{S} \cdot \mathfrak{S} \frac{\partial}{\partial \mathfrak{S}} \log g_t \right) \\ &+ \sum_r \bar{N}_r \left(\log \frac{h_r b_r}{N_r \sigma_r} + 1 + \log 1/\mathfrak{S} \cdot \mathfrak{S} \frac{\partial}{\partial \mathfrak{S}} \log \frac{h_r b_r}{\sigma_r} \right), \\ &= \sum_t \bar{M}_t \left(\log \frac{g_t}{\bar{M}_t} + 1 \right) + \sum_r N_r \left(\log \frac{h_r b_r}{N_r \sigma_r} + 1 \right) \\ &+ (E + \sum_r N_r \chi_r) \log 1/\mathfrak{S}. \quad (3.4) \end{aligned}$$

The expected terms in $\mathfrak{S}^{X_r}$ in (3.4) cancel.

For the vapour of a solid (crystal) in equilibrium with the solid, similar considerations apply. If we assume for simplicity that the external fields of force affect only the vapour molecules, we find at once by arguments similar to those above that

$$\begin{aligned} dQ = \frac{1}{\log 1/\mathfrak{S}} \left\{ X d \left(\log K + \log 1/\mathfrak{S} \cdot \mathfrak{S} \frac{\partial}{\partial \mathfrak{S}} \log K \right) \right. \\ \left. + d \left(\bar{N} + \log 1/\mathfrak{S} \cdot \mathfrak{S} \frac{\partial \bar{N}}{\partial \mathfrak{S}} \right) \right\}. \end{aligned}$$

There exists, therefore, the required function S , given by

$$(S - S_0)/k = X \log K(\vartheta) + \bar{N} + E \log 1/\vartheta. \quad (3.5)$$

This can be put into a form analogous to (3.4) with the help of (2.53). We obtain

$$\begin{aligned} (S - S_0)/k = (X - \bar{N}) \left\{ \log K(\vartheta) + \log 1/\vartheta \cdot \vartheta \frac{\partial}{\partial \vartheta} \log K(\vartheta) \right\} \\ + N \left\{ \log \frac{h(\vartheta)b(\vartheta)}{N\sigma} + 1 + \log 1/\vartheta \cdot \vartheta \frac{\partial}{\partial \vartheta} \log \frac{h(\vartheta)b(\vartheta)}{\sigma} \right\} \end{aligned} \quad (3.51)$$

$$\begin{aligned} = (X - \bar{N}) \log K(\vartheta) + \bar{N} \left(\log \frac{h(\vartheta)b(\vartheta)}{N\sigma} + 1 \right) \\ + (E - N\chi) \log 1/\vartheta. \end{aligned} \quad (3.52)$$

The analogy between (3.4) and (3.51) is now complete since $X - \bar{N}$ is the number of molecules in the crystal and χ is defined in opposite senses in the two cases.

We can now, by comparison of (3.4) and (3.51), see that each particular constituent makes a definite independent contribution to the entropy. The contribution of the body of gaseous molecules of type r is in both cases

$$N_r k \left[\log \left\{ \frac{h_r(\vartheta)b_r(\vartheta)}{N_r \sigma_r} \right\} + 1 + \log 1/\vartheta \cdot \vartheta \frac{\partial}{\partial \vartheta} \log \left\{ \frac{h_r(\vartheta)b_r(\vartheta)}{\sigma_r} \right\} \right]. \quad (3.6)$$

The contribution of a crystal of M molecules is

$$M k \left[\log K(\vartheta) + \log 1/\vartheta \cdot \vartheta \frac{\partial}{\partial \vartheta} \log K(\vartheta) \right]. \quad (3.61)$$

The entropy of the whole assembly of which these may be constituent parts contains an indeterminate constant, but this constant cannot depend on any parameter appearing in (3.6) or (3.61). The formal dependence of these expressions on the number of systems (N , M) is now fully specified, because we have considered systems in which the numbers of constituents can be reversibly changed*.

It is further clear that the molecules of type r make the contribution (3.6) to the entropy of any assembly in statistical equilibrium in which there are N_r molecules in a volume V at temperature ϑ . If we think of such an assembly in which the possibility of dissociation is

* Ehrenfest and Trkal, *loc. cit.* p. 163.

temporarily suspended, so that the assembly is in statistical equilibrium with the N's and M's fixed, the contribution to the entropy made by the r th type of molecule can be regarded as still given by (3.6).

In addition to the unspecified constant in the entropy of the whole assembly, the entropy contributions of the various species are not quite as absolute as they appear to be, for they depend on the precise convention by which unit weight is assigned. That is to say, they really contain an unspecified multiple of M or N. A change in this convention will change the values of the entropy contributions, but in such a way as to make no difference to any physical result. Whether or no we admit the idea of absolute entropy, these formulæ for the entropy contributions which we have just obtained are all that can be required in actual argument.

§ 4. *Use of the characteristic function.*—As we have already shown for non-dissociating assemblies, the connexion between thermodynamics and statistical mechanics can be simplified by the use of Planck's Characteristic Function Ψ as the primary thermodynamic quantity. Ψ is defined in thermodynamics by the equation $\Psi = S - E/T$, and has the properties

$$E = T^2 \frac{\partial \Psi}{\partial T}, \quad S = \Psi + T \frac{\partial \Psi}{\partial T}, \quad Y_1 = T \frac{\partial \Psi}{\partial y_1}. \quad (4.1)$$

In order to make Ψ fundamental, we recall the integral for C (2.24), and it is evident that we have only to define Ψ in such a way that

$$C = \frac{1}{2\pi i} \int_{\gamma} \frac{dz}{z^{E+1}} e^{\Psi(z)k}; \quad \dots \quad (4.2)$$

the thermodynamic theorems follow at once.

To make a simple definition, we use the fact that all the details of the distribution laws for the assembly, including to a sufficient approximation the value of C, are the same as if the M's and N's are fixed at their equilibrium values. The number of such examples of the assembly is

$$\frac{X_1! \dots X_s!}{\bar{M}_1! \dots \bar{M}_s! \bar{N}_1! \dots \bar{N}_j! \sigma_1^{\bar{N}_1} \dots \sigma_j^{\bar{N}_j}}$$

DEFINITION. *The characteristic function of an assembly is k times the sum of the logarithms of the partition functions of all the component systems in the assembly plus the logarithm*

of the number of possible examples of the assembly, when the numbers of the various systems have their equilibrium values and the argument of the partition functions is $\mathfrak{S} = e^{-1/kT}$.

It is not conveniently possible to avoid making the identification of $\mathfrak{S}$ and $e^{-1/kT}$ part of the definition. No attempt to use the first equation in (4.1) as a means of connecting $\mathfrak{S}$ and T , on the assumption that we know E and Ψ as functions of $\mathfrak{S}$, can possibly succeed in making T precise—a difficulty pointed out in § 6 of the second paper.

According to these definitions, we find for the two types of assembly we are discussing :

$$(\Psi - \Psi_0)/k = \sum_t M_t \left(\log \frac{g_t}{M_t} + 1 \right) + \sum_r \bar{N}_r \left(\log \frac{h_r b_r}{\bar{N}_r \sigma_r \mathfrak{S}^{\chi_r}} + 1 \right), \quad (4.3)$$

$$(\Psi - \Psi_0)/k = X \log K(\mathfrak{S}) + \bar{N}, \quad (4.4)$$

$$= (X - \bar{N}) \log K(\mathfrak{S}) + \bar{N} \left(\log \frac{hb}{\bar{N} \sigma \mathfrak{S}^{-\chi}} + 1 \right). \quad (4.41)$$

These definitions actually determine the value of the constants Ψ_0 , and therewith S_0 , for $\Psi_0 = S_0$, though the values of these constants are immaterial. In fact, with sufficient accuracy,

$$\Psi_0/k = \sum_t (X_t \log X_t - X_t)$$

in (4.3), (4.4), or (4.41).

§ 5. *The usual introduction of entropy into statistical mechanics and the "increasing property" of entropy.*—In ordinary presentations of entropy in statistical mechanics the property of entropy which is taken as fundamental is its "increasing property." This presentation has already been critically considered*, but we can now push the analysis somewhat further.

Properly enunciated, the postulate of the increasing property is equivalent to some such statement as the following :—

(1) If an assembly in statistical equilibrium is divided into two parts by some such workless process as the closing of an ideal door, the sum of the entropies $S_1 + S_2$ for the two parts after separation is equal to the entropy S_{12} of the whole before separation.

(2) If two assemblies separately in equilibrium are joined together into one assembly in a similar way, the joint

* Second paper. § 4.

assembly takes up a new equilibrium in which $S_{12} \geq S_1 + S_2$, equality being only possible under certain special conditions of equal temperatures and concentrations.

It has already been shown for less general assemblies * that no introduction of entropy on the basis of this postulate can lead without ambiguity to the absolute temperature scale. These arguments are equally valid here in the general case. It was shown further that the least objectionable definition of entropy from this standpoint is a definition of "kinetic entropy" as k times the logarithm of the number of weighted complexions representing the specified state of the assembly. Kinetic entropy is a fluctuating quantity. If, as usual, a non-fluctuating quantity is required, it was shown that we may best define the "statistical entropy" as k times the logarithm of the total, average, or maximum number of weighted complexions. These numbers are indistinguishable from each other and from $k \log C$. In the previous case such a definition is reasonably satisfactory, as it provides naturally a function S which has the desired increasing property for simple cases of junction, in which the separate assemblies can after junction exchange energy only, so that only their temperature can change. This S does in fact agree with the entropy of thermodynamics so long as the number of systems in a group does not change. Junctions resulting in changes of volume, for example, were not considered. For such junctions the function $k \log C$ as defined in the simple case does not possess the required increasing property.

To discuss general cases of junction, we must be prepared to allow changes in the number of systems in a group. Such changes can take place in a dissociating assembly, and a definition should therefore now be possible on these lines. If, as before, we take $k \log C$ for the statistical entropy, we obtain an expression which agrees with (3.41) in its variable part and assigns to S_0 the value Ψ_0 of § 4. We shall show in the next section that the variable part of S does now in fact possess the increasing property in all circumstances, but it is obvious that the complete $k \log C$ does not. It follows that $k \log C$, *if we drop the constant term*, is a suitable definition for S . But the need to eliminate this constant term means that there is now no entirely natural definition of this sort which can at once be shown to possess the increasing property.

* Second paper, § 6.

It is now well to consider somewhat more closely the implications of postulating the increasing property as the fundamental property of entropy. It implies in particular that the entropy of two gram-molecules of a gas X must be twice that of one gram-molecule at the same temperature and concentration. This is as it should be (in agreement with § 3) when the two gram-molecules or one gram-molecule are both parts of the same assembly in which the amount of X present can be reversibly changed. But the postulate asserts it in all cases, and asserts in general that entropies must be directly comparable whether or not they correspond to states which can be connected by a reversible process. There is no need whatever that this should be so. In asserting it, we are actually going a long way towards asserting the existence of *absolute entropy* and making a special choice of the constant S_0 for the assembly and each of its parts. It is not therefore surprising that there is no natural method of defining S , constant and all, in such a way that the increasing property is satisfied.

If we accept the position that the constant terms in the entropy are meaningless and need not satisfy the increasing property, then $k \log C$ retains its suitability for a definition of statistical entropy. We have already seen that it agrees with S as introduced by the classical method of § 3. But $k \log C$ has of course the usual wider range of validity in that it applies to and defines the entropy for statistical states of the assembly which are in no sense equilibrium states. It is perhaps chiefly to obtain this generalization of entropy that entropy has been introduced so often into statistical mechanics, as k times the logarithm of the "thermodynamic probability." The increasing property has been used as the simplest way of making this introduction plausible, and (probably) not from any real sense of its more fundamental character. When this generalization is required, my own attitude is that entropy is best defined outright as $k \log C$ and justified by comparison with S introduced as in § 3.

Whether we prefer to take the increasing property as fundamental or as a deduction, the fact that, suitably defined, the entropy possesses it is interesting and important. We give the necessary proofs in the next section.

§ 6. *Proof of the increasing property.*—It is simplest to discuss the problem of junction in two stages. Consider a dissociating assembly in equilibrium, for which the external

forces represent only the retaining walls of the enclosure containing it. With $S_0=0$, the entropy is given by

$$S_1/k = \sum_t M_1 \left(\log \frac{g_1}{M_1} + 1 \right) + \sum_r N_1 \left(\log \frac{h_1 b_r}{N_1 \sigma_r} + 1 \right) + (E_1 + \sum_r N_1 \chi_r) \log 1/\vartheta_1, \quad (6.1)$$

and the temperature ϑ_1 is given in terms of E_1 by an equation equivalent to $\partial S_1/\partial \vartheta_1=0$. For convenience the suffixes t and r are temporarily omitted from the M 's, N 's, g 's, and h 's which require a suffix 1 or 2 to distinguish the two assemblies, and the bars are dropped. A similar expression gives the entropy of the second assembly. When the assemblies are joined, the M 's and N 's will in general change. It will not affect, however, the final inequality if we suppose to start with that on junction all the M 's and N 's remain fixed. For such an assembly we can calculate an intermediate function * s_{12} , which has the same form as S_{12} with the artificial values of the M 's and N 's. This is the first stage. In the second stage we suppose the M 's and N 's to change to their equilibrium values when the entropy is S_{12} .

At the end of the first stage we have therefore

$$\begin{aligned} s_{12}/k &= \sum_t (M_1 + M_2) \left(\log \frac{g_{12}}{M_1 + M_2} + 1 \right) \\ &+ \sum_r (N_1 + N_2) \left(\log \frac{h_{12} b}{(N_1 + N_2) \sigma_r} + 1 \right) \\ &+ [(E_1 + E_2 + \sum_r (N_1 + N_2) \chi_r)] \log 1/\vartheta_{12}. \quad (6.11) \end{aligned}$$

In this equation we are to suppose, as is always possible, that ϑ_{12} is determined in terms of $E_1 + E_2$ by the standard equation (2.41), which is equivalent to

$$\partial s_{12}/\partial \vartheta_{12} = 0. \quad . \quad . \quad . \quad . \quad (6.12)$$

Consider the value of $(s_{12} - S_1 - S_2)/k$, taking separately the terms dependent on the volumes † V_1 , V_2 , and V_{12} , and on ϑ_1 , ϑ_2 , and ϑ_{12} . The volume terms consist of a set of terms of the form

$$f = (M_1 + M_2) \log \frac{V_1 + V_2}{M_1 + M_2} - M_1 \log \frac{V_1}{M_1} - M_2 \log \frac{V_2}{M_2}. \quad (6.2)$$

* If we accept a definition based on $k \log C$ for the entropy, then s_{12} is itself the entropy, and the statement of the proofs of this section can be slightly simplified.

† There is no reason to suppose that the volumes are the same for all different molecular species in the two assemblies. So far as different volumes can be obtained by semi-permeable membranes, they can be supposed to occur in these formulæ. Thus $(g_t)_1$ contains the factor $(V_t)_1$ etc.

Now $f'=0$ when $M_1/V_1=M_2/V_2$, and

$$\frac{\partial f'}{\partial M_1} = \log \frac{V_1 + V_2}{M_1 + M_2} - \log \frac{V_1}{M_1};$$

so that $\partial f'/\partial M_1=0$ when $M_1/V_1=M_2/V_2$. Finally

$$\frac{\partial^2 f'}{\partial M_1^2} = -\frac{1}{M_1 + M_2} + \frac{1}{M_1} \geq 0.$$

Thus in all cases $f' \geq 0$, and equality can only hold when $M_1/V_1=M_2/V_2$. The argument applies to each term of the set.

Consider next the $\mathfrak{S}$ -terms. These are of exactly the same form as in the simple case of non-dissociating assemblies, and the argument of the former paper applies. It follows therefore that

$$s_{12} \geq \mathfrak{S}_1 + \mathfrak{S}_2$$

in all cases, and that the equality can hold if and only if

$$(M_t/V_t)_1 = (M_t/V_t)_2, \quad (t=1, \dots, s), \quad . \quad (6.31)$$

$$(N_r/V_r)_1 = (N_r/V_r)_2, \quad (r=1, \dots, j), \quad . \quad (6.32)$$

$$\mathfrak{S}_1 = \mathfrak{S}_2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (6.33)$$

If (6.31), (6.32), and (6.33) are all satisfied, then

$$\mathfrak{S}_1 = \mathfrak{S}_2 = \mathfrak{S}_{12}.$$

In the second stage we have a single assembly, for which we can drop the suffixes 1, 2, and a function s of the state of that assembly which is given by the same formula as S for the final equilibrium state. The only difference is that in general the values of the M 's and N 's are not the equilibrium values. As the M 's and N 's change subject to (2.23), $\mathfrak{S}$ will also change subject throughout to (6.12). Thus

$$\begin{aligned} \frac{ds}{dN_r} &= \frac{\partial s}{\partial N_r} + \sum_t \frac{\partial s}{\partial M_t} \frac{\partial M_t}{\partial N_r} + \frac{\partial s}{\partial \mathfrak{S}} \frac{\partial \mathfrak{S}}{\partial N_r} = \frac{\partial s}{\partial N_r} + \sum_t \frac{\partial s}{\partial M_t} \frac{\partial M_t}{\partial N_r} \\ &= \log \frac{\beta_r M_1^{q_{1r}} \dots M^{q_{sr}}}{N_r}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (6.4) \end{aligned}$$

When the N 's have their correct equilibrium values,

$ds/dN_r=0$. Further,

$$\begin{aligned}\frac{d^2s}{dN_r^2} &= -\frac{1}{N_r} - \sum_t \frac{q_{tr}^2}{M_t} + \frac{\partial}{\partial s} \log \beta_r \frac{\partial s}{\partial N_r}, \\ &= -\frac{1}{N_r} - \sum_t \frac{q_{tr}^2}{M_t} - \frac{\left(s \frac{\partial}{\partial s} \log \beta_r \right)^2}{s \frac{\partial E}{\partial s}} < 0; \\ \frac{d^2s}{dN_r dN_{r'}} &= -\sum_t \frac{q_{tr} q_{tr'}}{M_t} - \frac{\left(s \frac{\partial}{\partial s} \log \beta_r \right) \left(s \frac{\partial}{\partial s} \log \beta_{r'} \right)}{s \frac{\partial E}{\partial s}}.\end{aligned}$$

It easily follows that the second-order terms in an expansion of s in the neighbourhood of its correct equilibrium value S can be expressed as a set of square terms all with negative coefficients, and that therefore $s-S$ is essentially negative. The second stage can therefore only result in a further increase of S_{12} over $S_1 + S_2$.

We have therefore established, with a suitable definition of S , the relation

$$S_{12} \geq S_1 + S_2.$$

It remains only to show that the conditions (6.31), (6.32), and (6.33) are sufficient for actual equality, and for this it is only necessary to show that under these conditions the changes of the second stage are nil. The conditions that determine the M 's and N 's in any assembly, written in full, are

$$\frac{M_1^{q_{1r}} \dots M_s^{q_{sr}}}{\{g_1(s)\}^{q_{1r}} \dots \{g_s(s)\}^{q_{sr}}} = \frac{N_r \sigma_r s^{x_r}}{h_r(s) b_r(s)}, \quad \dots \quad (6.5)$$

and for any value of r and t

$$g_t(s) = V_t G_t(s), \quad h_r(s) = V_r H_r(s),$$

where in $G_t(s)$ and $H_r(s)$ s is the sole variable. If, therefore, (6.5) is satisfied for the separate assemblies before junction, and the conditions (6.31), (6.32), and (6.33) are satisfied, (6.5) will still be satisfied for the complete assembly after junction, which will therefore be in its equilibrium state without further change. The second process therefore vanishes, and we have the equality

$$S_{12} = S_1 + S_2. \quad \dots \quad (6.6)$$

These conditions are therefore both necessary and sufficient.

If we carry out the converse process and divide the

assembly into two separate parts, the same conditions will be automatically satisfied, ignoring fluctuations, and so the equality (6.6) is necessarily valid. The deduction of the increasing property of S for assemblies in statistical equilibrium is thus completed.

An exactly similar proof holds for the entropy of the vapour-solid combination in equilibrium.

§ 7. *Nernst's Heat Theorem and the Chemical Constants.*—Nernst's Heat Theorem may be enunciated in the following form:—*In a "condensed system" the change of entropy in any isothermal reversible process tends to zero as the temperature tends to zero.* For any "condensed system" for which we can construct the partition function we can examine the position of Nernst's Theorem in statistical theory. Suppose first that the partition function for one molecule before and after the reaction has respectively the simple form

$$\sum_r p_r \mathfrak{S}^{\epsilon_r}, \quad \sum_r q_r \mathfrak{S}^{\eta_r}.$$

All the degrees of freedom are thus thought of as of one type, and their total number can never be changed by any reaction. Now the contribution to the entropy of the assembly made up of N molecules of the substance in either form is

$$Nk \left[\log f(\mathfrak{S}) + \log 1/\mathfrak{S} \cdot \mathfrak{S} \frac{\partial}{\partial \mathfrak{S}} \log f(\mathfrak{S}) \right],$$

where f is the partition function. As $\mathfrak{S} \rightarrow 0$, this tends to

$$Nk \left[\log p_0 \mathfrak{S}^{\epsilon_0} + \log 1/\mathfrak{S} \cdot \mathfrak{S} \frac{\partial}{\partial \mathfrak{S}} \log p_0 \mathfrak{S}^{\epsilon_0} \right] = Nk \log p_0$$

before the reaction, or $Nk \log q_0$ after the reaction. Thus Nernst's Theorem is equivalent to the statement that *the weights of the lowest quantum states must be equal**. If, and only if, this is the case, then Nernst's Theorem follows at once as a direct consequence of statistical theory. There is no need for any appeal to the conception of *absolute* entropy.

The simple case examined above hardly corresponds to actual facts. An important real case which we can examine is that of a reaction between solids in the crystalline form †.

* This result was pointed out in a preliminary way in the Second paper, § 8.

† The actual reaction may, if necessary, be supposed to take place in a vapour phase present in negligible quantity in the assembly.

The contribution to the entropy of the assembly of any crystal containing any molecules is

$$Nk \left[\log K(\mathfrak{S}) + \log 1/\mathfrak{S} \cdot \mathfrak{S} \frac{\partial}{\partial \mathfrak{S}} \log K(\mathfrak{S}) \right].$$

It can be shown* that Born's† results on the mean energy of a crystal can be translated at once into results on partition functions. If we ignore the possible ultra-violet absorption frequencies of the crystal due to the motion of the electrons‡ as distinct from the complete atoms, we find

$$\log K(\mathfrak{S}) = - \frac{3}{(\log 1/\mathfrak{S})^3} \sum_{j=1}^3 \frac{1}{k^3 \Theta_j^3} \int_0^{k\Theta_j \log 1/\mathfrak{S}} x^2 \log(1 - e^{-x}) dx \\ - \sum_{j=4}^{3(n-1)} \log(1 - \mathfrak{S}^{h_{vj}}), \quad . \quad . \quad . \quad (7.1)$$

where n is the number of atoms in an elementary cell of the crystal lattice, and the Θ_j , v_j are constants characteristic of the crystal. We must interpret the molecule in the crystalline state for the purposes of this formula as the collection of all the atoms in one elementary cell.

When $\mathfrak{S} \rightarrow 0$,

$$k\Theta_j \log 1/\mathfrak{S} \rightarrow \infty,$$

and

$$\int_0^{k\Theta_j \log 1/\mathfrak{S}} x^2 \log(1 - e^{-x}) dx \rightarrow \int_0^\infty x^2 \log(1 - e^{-x}) dx = 2 \sum_{n=1}^\infty \frac{1}{n^4} = \frac{\pi^4}{45}.$$

The second set of terms all tend to zero like a power of $\mathfrak{S}$, and thus except for a constant multiple $\log K(\mathfrak{S})$ behaves like

$$\frac{1}{(\log 1/\mathfrak{S})^3}.$$

Both terms in the entropy therefore tend to zero as $\mathfrak{S} \rightarrow 0$, and as the entropy contributions all vanish, their difference vanishes and Nernst's Heat Theorem holds for all such reactions.

It is important, however, to look somewhat more closely into this result. Formula (7.1), on which it depends, is based on the usual analysis into normal coordinates of the motion of a dynamical system executing small vibrations.

* Darwin and Fowler, Proc. Camb. Phil. Soc. *loc. cit.*

† 'Der Dynamik der Krystalgitter,' Chap. 5.

‡ It is correct to do so here, for we consider the atoms as the structural units in this discussion. The internal mechanism and construction of the atoms we must ignore consistently throughout.

Each such coordinate is treated like Planck's line vibrator, and its lowest quantum state (of zero energy) is assigned the weight unity. The result, however, cannot and does not depend on this convention. If we assign the weight p_0 to such a state, keeping of course relative weights unaltered, the expression (7.1) for $\log K(\mathfrak{S})$ will be altered by the addition of the term

$$3n \log p_0.$$

The entropy is altered by the addition of the term

$$3Nn \log p_0, \quad . \quad . \quad . \quad . \quad . \quad (7.2)$$

where Nn is the number of atoms in the crystal, and (7.2) is now the limit of the entropy as $\mathfrak{S} \rightarrow 0$. This does not in any way affect the vanishing of the entropy *change* as $\mathfrak{S} \rightarrow 0$, for, as the total number of atoms cannot alter, the same constant limit must occur in both the values of the entropy before and after the reaction*.

Nernst's Heat Theorem for reactions between crystals is therefore, on the general principles of the quantum theory, a deduction from the fact that the weights of the lowest quantum states of such systems are necessarily equal. This equality is a result of the form into which the internal motions of the crystals can be analysed. It is not yet possible to establish fully the validity of the theorem on the same basis for other types of condensed systems—liquids and supercooled liquids (glasses)—in the absence of suitable partition functions. It is, however, not unreasonable to suppose that its truth ultimately rests on the same analysis of the internal motion into normal modes and the same consequent equality of the weights of the lowest quantum states.

A particular use of Nernst's Theorem is to deduce the form of dissociation-equilibria in gases, from the vapour-pressure equation of each gas, showing in particular that the constant in the equation of dissociation-equilibrium can be expressed in terms of the constants in the vapour-pressure equations, the so-called chemical constants. It is, in fact, on account of this property that the chemical constants earn their name. It has been shown in the third paper† that this property can be most naturally

* It is presumably not even necessary to assign the same weight to the lowest quantum state of different kinds of atoms executing simple harmonic vibrations. The weights for any one kind of atom must of course be the same in all crystals. But I have not examined this point in detail.

† In generalization of a similar theorem due to Ehrenfest and Trkal, *loc. cit.*

established directly as a theorem in statistical mechanics without appeal to Nernst's Theorem. It is now clear that both this property and Nernst's Theorem itself are consequences of the same facts: namely, the particular behaviour of the partition function for any crystal, and probably for other solids and liquids as well, as $T \rightarrow 0$.

Summary.—Finally, one may perhaps briefly re-state the central idea of the series of papers here concluded. We have approached the subject of statistical equilibrium from the standpoint that its characteristics are determined by the *average* values of certain quantities taken over all dynamically possible states of an assembly—all states, that is to say, with the given total energy. It has been found possible to work out the details of the equilibria in fairly general cases without any appeal to thermodynamical ideas. The position is maintained that such ideas are really irrelevant in statistical theory except for the logical introduction of the absolute temperature, and the ordinary introduction of entropy into statistical theory is criticized. At the same time the fact that the laws of thermodynamics are deductions from the theory is important, and has been established for all the assemblies discussed.

LIV. *Electrical Properties of a Flint Glass of Density 6.01.*
By G. L. ADDENBROOKE *.

IN a Royal Society paper (Phil. Trans., 1878) Hopkinson described measurements of the specific inductive capacities or dielectric constants of four kinds of Flint Glass of increasing densities, which have since been quoted in tables of constants.

He ends his paper as follows:—

“If the electrostatic capacities (K) be divided by the density (D) we find the following quotients:—

	D.	K.	$\frac{K}{D}$.	Refractive index D line.
Very light Flint ...	2.87	6.57	2.29	1.541
Light Flint	3.2	6.85	2.14	1.574
Dense Flint	3.66	7.4	2.02	1.622
Double extra dense..	4.5	(10.1) (9.98)	(2.25) (2.22)	1.710

* Communicated by the Author.

"Thus $\frac{K}{D}$ is not vastly different from a constant quantity.

"Messrs. Gibson and Barclay find for paraffin 1.977 : taking the density of paraffin as 0.93, we have the quotient of 2.13. This empirical result cannot of course be generally true, or the capacity of a substance of small density would be less than unity."

Dielectric Constants of Heavier Glasses.

The glass of the greatest density examined by Hopkinson was 4.5. In 1909, Thornton made measurements on an ellipsoid of glass of density 4.65 (Proc. Royal Soc., 1909). The dielectric constant of this he gives as 10.64. In his paper he puts Hopkinson's and his own results in the form of a curve, which is reproduced and extended below.

Shortly after the publication of Thornton's paper, Messrs. Hilger informed me that there was a glass of 4.85 density obtainable, from which they could cut a thin sheet 6 inches square. I obtained such a sheet and measured its dielectric constant, in 1911, by an alternating-current method, comparing it with a standard air-condenser. The constant 11.2 was again higher and fitted in with a prolongation of Thornton's curve. Unfortunately it was broken before the final corrections could be made. At the same time I found that at the Jena factory they made a glass of about 6 density. Messrs. Hilger, however, stated that they could not get this in a size from which they could cut a disk more than 4 inches in diameter.

I thought this too small at the time to get good results, having regard also to the risks of breakage and cost ; but it occurred to me that a test might be made of the glass in the form of fragments by a method of mixture, and Messrs. Hilger were good enough to procure for me some lumps of the glass.

The particulars are as follows :—

Properties of Dense Silica Flint.

Refractive Index for D-line.	Medium disp. C-F line.	Density
1.9201	0.04381	6.01

Approximate Composition SiO 22% ; PbO, 78%.

The glass has a decidedly yellow tinge but otherwise is quite transparent. Exposed since in the laboratory for some ten years, the surface shows slight traces of action, but a little protection would evidently have obviated this.

Judging by its density and composition, the density of natural silica being 2·61, fused silica 2·0, and lead 19·2, it must contain over 30 per cent. by volume of metallic lead. It breaks easily, though hard. It softens and melts at a fairly low red-heat without showing any signs of blackening. That such a composition should be perfectly transparent and a high-class insulator is remarkable enough in itself.

Other matters prevented me going further with this glass at the time, and the war coming on, it was not until lately that I was able to do more with it.

In the meantime I found that the method of mixture had been used by Thwing to obtain the dielectric constants of a number of substances in fragments or powder form and that his results were accepted by writers of works of reference (*Physical Review*, July–Aug. 1894). Thwing does not give any details beyond the formula, but as there are several points of importance which need attention to secure accuracy, a memorandum is here appended dealing with them. In view of the great improvements and facilities for measuring small capacities which have become available during the last few years, the method is readily workable and could be employed for the measurement of the electrical properties of a number of substances of which at present little is known.

As the result of several trials, the dielectric constant of the above glass of density 6 was finally found to be 13, within from 2 to 3 per cent.

So far as I am aware this is not only the highest dielectric constant yet found for any glass, but it is the highest found for any material not of abnormal character and not complicated by the effects of absorption. Apparently also, the glass in question is the substance for which the deviation from Maxwell's relation of the dielectric constant to the square of the refractive index is greatest, when uncomplicated by the effects of absorption.

The data are given below for the range of glasses:—

Relation of K to the Square of Refractive Index.

	(1)	(2)	(3)	(4)	(5)	(6)
Density.....	2·87	3·2	3·66	4·12	4·5	6·01
K	6·57	6·85	7·4	8·52	9·98	13·0
N ²	2·35	2·45	2·58	2·85	3·0	3·68
K/N ²	2·8	2·75	2·86	3·0	3·33	3·55

The specimen of glass of density 6 is not quite the densest known, there is another (see *Smithsonian Tables*, 1910, p. 180) of a density of 6·33. The composition of this is given as SiO₂ 21·9 per cent., PbO 78 per cent., and traces of arsenic.

Now there is a definite chemical compound known as PbSiO_3 . If a calculation is made of the respective weights of its components, it would appear to be composed of PbO 78.6 per cent. and SiO_2 21.4 per cent. Consequently, this densest glass corresponds with the chemical compound PbSiO_3 with a small fraction of silica dissolved or mixed in it, and the specimen under discussion with a density of 6 may consist essentially of this compound *plus* a fraction more silica.

Mr. Frink, the director of the Glass Research Association, informs me that with these very dense glasses the difficulty is to prevent this compound crystallizing out, and hence the great importance of stirring. He has given me a small specimen of this compound, and offered to try and obtain sufficient of it in a pure state to enable its electrical properties to be determined. A test on such a specimen would complete the investigation. It does not seem probable that its properties would differ appreciably from those of the glass of 6.33 density, the refractive index of which is 1.96.

All these glasses are essentially a mixture of silica and lead oxide. Since the constituents can form a definite compound, apparently this compound will be formed as far as the proportions admit, and then this compound is dissolved in the remaining free silica, or mechanically mixed with it, each aggregate probably retaining essentially its physical properties.

Note.—Since writing the above Mr. Frink has further pointed out to me that, if a specimen of heavy glass has crystallized out, and the crystals are examined with a good magnifying glass, it will be found that mixed with the usual form of the crystals there are a certain number of others, of the same order, but of a more elongated shape and with certain other slight differences, which point to there being present a second slightly different silicate of lead. It might therefore be that all the Silica is divided up between these two compounds.

Thus the glass of density 6 seems to be very near the limit of what can be done by mixture, so that we are near the end of a definite series, and its electrical and optical properties should closely approximate those of the definite chemical compound. It will be noted that the relation of K to N^2 continually increases. It may be that the final density of 6.33, which has been attained is due to a reduction of volume on crystallization, as natural quartz is denser than fused silica, rather than to a correspondingly higher proportion of lead.

*Observations on Curves showing results for
the Series of Flint Glasses.**Electrical Properties.*

Having now dealt with these matters it is interesting to plot for the series of glasses Hopkinson's and Thornton's results with the new determination.

Mr. Dye, of the N. P. L., has also drawn my attention to a communication to the *Jahrbuch Zeitschrift für Drahtlose Telegraphie und Telephonie* for August 1921, in which E. Schott gives a new set of determinations of the dielectric constants of Jena glasses. The glass with the highest constant included in it is No. 198*b*. Having a dielectric constant of 11.3 and refractive index 1.77, this is evidently the same glass of density slightly under 5 mentioned by me above for which I found a dielectric constant of about 11.2.

I understand that since the war there has been a difficulty in making the glass of density which forms the subject of this communication, and that it is not at present procurable.

Three of Schott's results are inserted in the diagram. It will be seen that they agree well with Hopkinson's and Thornton's, and thus confirm them and the general character of the curve.

The left-hand curve in the diagram covers the relation of density to K or rather to $(K-1)$. (On this point see Addenbrooke, Faraday Soc. Proceedings, Dec. 1919.) The values of the $(K-1)$ of these glasses lie in a curve of which a line drawn from the densest—or what we may venture to take as approximating the $(K-1)$ of the chemical compound—seems to form the axis. This point I hope to show later has considerable significance.

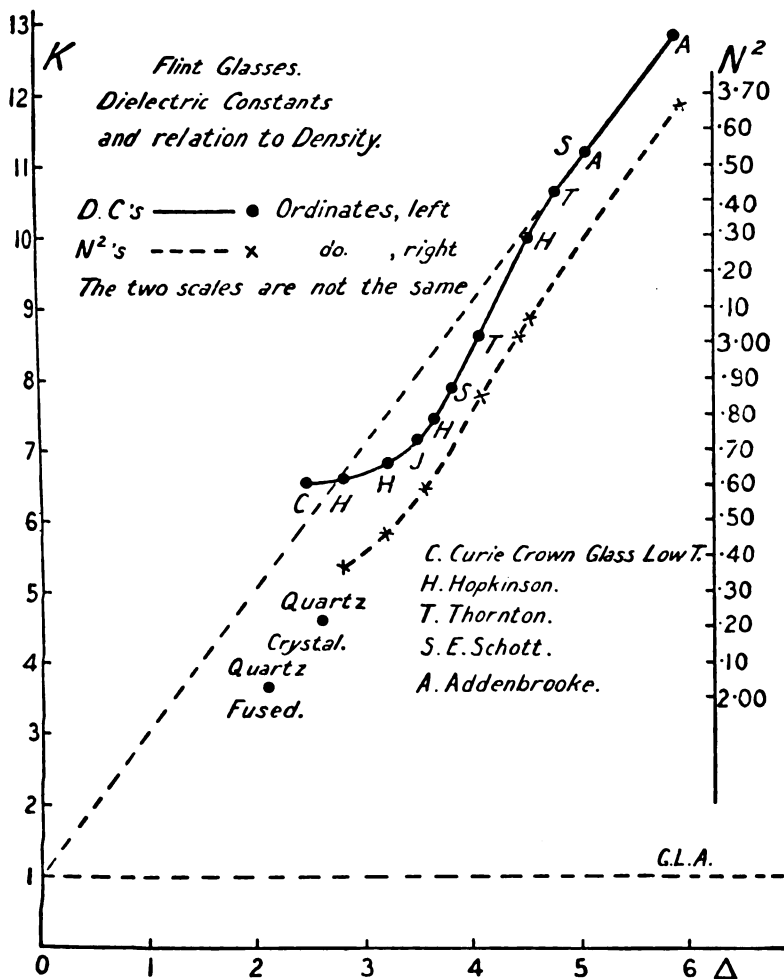
In considering the curves and data, as the electrical properties are volume properties, it is important to bear in mind the great differences in volume covered by different proportions in weight of the various constituents.

According to Pulfrich's analysis (French Physical Society Tables) all the glasses of lower density have either potash or soda in their composition, also possibly barium, but as the density increases they are more and more completely composed of lead oxide and silica. The composition of Hopkinson's glasses is unknown, but probably silica does not differ much from that of the Jena glasses.

The above analysis of the composition of these glasses is given in percentages of PbO and SiO_2 . There appears to be some doubt amongst chemists as to how far these glasses are mixtures of these compounds or are increasingly $PbSiO_3$.

plus SiO_2 . From work on the relation of the dielectric constants of substances to their other physical properties the evidence seems to me strongly in favour of chemical combination, and also against the inference that either lead or

Fig. 1.



dissolved lead oxide has a specially high dielectric constant. The raising of the dielectric constant so high is the result of chemical combination. It would, however, take up too much space to give here the further evidence on which these views are formed.

Optical Properties.

In the above diagram with ordinates on the right side, there is given for comparison a curve of the squares of the refractive indices for these glasses. It will be seen that the inflexion of the lower part of the curve is also shown in this, though naturally to a less degree, and on a different scale.

Details of the methods by which the above results were obtained are appended below.

The method of obtaining Dielectric Constants of Substances in Mixture.

The method consists in forming an air-condenser with metal electrodes of known area, say 250 sq. cm. spaced, say, 2 to 5 mm. apart. This air-condenser, being in the form of a box with open top, can be filled with granules or powder of any material to be investigated.

If the density of the material is known, the volume which fills the container can be found by adding previously weighed portions, and no filling with a second substance is necessary.

If, however, the density of the substance is not known or it is desired for other purposes not to expose the material to the air, then a second liquid substance is added. In most cases, ordinary paraffin oil which has been dried by shaking up with powdered calcium carbide is convenient, and its dielectric constant can be taken as very close to 2.

From its dimensions we know the volume and area of the container.

The true air capacity of the condenser between electrodes is found from the dimensions, but as the thickness is small it is advisable to correct this by a calculation of the volume and area. The volume can be obtained very closely by first filling the container with liquid, say petrol, and then measuring the volume, after which the container can be dried before putting in the granules or powder.

The container is then filled with granules or powder. Paraffin oil is put in a litre measure-glass and its volume carefully noted. Oil is now poured into the container until it is full, after shaking to get rid of bubbles. The difference in the measure-glass gives the volume of oil needed; as an extra precaution the container may be put under a receiver and exhausted of air. Then

$$\text{Vol. container} - \text{vol. oil} = \text{vol. solid.}$$

I have mentioned the true air capacity of the condenser because much turns on this. It is insufficient to trust to

calculation alone. A careful electric measurement of the capacity of the condenser when empty must first be made in the position in which it is to be finally used; this of course includes all stray and other lines which do not pass directly between the electrodes, and this correction will be found very considerable: this is the chief point requiring special attention to secure accuracy.

We then have:

$$\text{Outside cap. of condenser} = \text{Measured air cap. of condenser} - \text{Calculated air capacity}$$

then

$$\text{True cap. of mixture} = \text{Measured cap. of mixture} - \text{Outside cap. of condenser}$$

and

$$K \text{ of mixture} = \frac{\text{True cap. of mixture}}{\text{Calculated air cap. of condenser}};$$

and this is the value of K , which should be used in Thwing's formula

$$K \text{ solid} = \frac{(\text{Vol. mix.} \times K \text{ mix.})(\text{Vol. liq.} \times K \text{ liq.})}{\text{Vol. solid}}.$$

The condenser or container was formed as follows:—

Two flat sheets of plate-glass and a length of square rubber cord of 5 mm. section were taken. The rubber cord, cut nearly through at the corners, was fixed to one sheet of glass with strong rubber solution so as to enclose an area, say, of 250 sq. cms., which was then coated with a thin varnish. When the varnish was nearly dry a stout sheet of tin-foil cut out to fit the area was laid on one side of the glass and pressed evenly down, the foil being left projecting at the upper edge to form a connexion.

A similar sheet of foil was fixed on one side of the other sheet of glass, and the two tin-foil electrodes were then held face to face in place by screw-clamps, the pressure on these being sufficient to reduce the space between the foil electrodes to 4.5 mm. For permanent use another insulator might be substituted for rubber which absorbs paraffin in time and swells.

Electrical Methods employed.

The current for the electrical measurements was provided by an oscillating valve arrangement G , which gave an alternating current at about 150 ~ and 1200 ~. Both frequencies were employed. A variable resistance of 100,000 ohms is shunted across the circuit, and this was adjusted until the voltage on

524 *Electrical Properties of a Flint Glass of Density 6.01.*

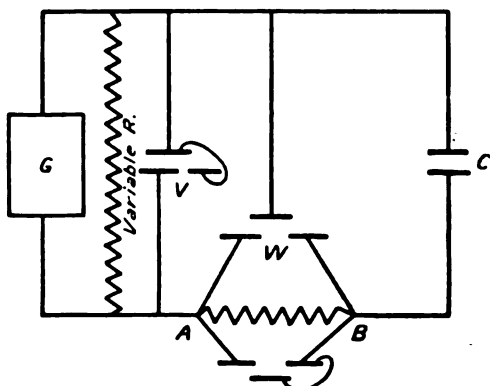
the condenser to be tested was maintained steadily at 110 volts, as shown by the electrostatic voltmeter *V* in the diagram.

G is the valve generating apparatus, *DE* the variable resistance of 100,000 ohms for regulating the circuit voltage.

V is the electrostatic voltmeter for preserving the P.D. across the circuit constant.

C is the condenser and *AB* a non-inductive resistance. Across this is a low reading electrostatic voltmeter which gave about 80 mm. deflexion for 1 volt between the terminals of *AB*, and the resistance of this being known therefore acts as an ammeter. *AB* was adjusted until a steady reading of about 200 mm. was obtainable on the ammeter.

Fig. 2.



The testing leads were now transferred from the condenser to a calibrated variable air-condenser, and the capacity of this was altered until the above reading was reproduced at the same voltage and frequency. The capacity indicated was then read off. It is free from capacity of the leads, is not influenced by any slight self-induction in *AB*, and though the valve should give nearly a sine wave, as the same wave form is used in both cases there should be no correction needed for this.

Measurements were first made on the empty condenser and then on the condenser filled, which gave the data for the calculations needed above.

Finally, before accepting the results, measurements under the same conditions were made with the electrostatic wattmeter.

The wattmeter *W* has a constant of about 40. That is,

with 110 volts on the needle, it gives a deflexion of about $\frac{110 \times 40}{10} = 440^\circ$ for 1/10 volt drop between the quadrants at

Unity power factor, or about 44° for a Power Factor of 1 per cent. at 1 volt drop across AB. I have already dealt with the working of this instrument on Low Power Factors (Electrician, Feb. 21, 1922).

This measurement, balancing out the capacity or reversible energy, gives separately the energy dissipated in leads, condenser itself, and the mixture; it also enables one to see that there is no abnormal leakage. The loss in this case was small, therefore the capacity measurement was practically free from the effects of absorption.

(As the result of long experience I find that absorption is always accompanied by dissipation of energy more or less directly proportionate to any increase of apparent capacity due to it. If, therefore, the loss is very small, being also at 90° phase difference with the capacity component of the current, we may conclude that the capacity found represents closely the true dielectric constant. See epitome of my lectures (Journal I. E. E. Jan. 1919, indexed under Institution Notes).

This method of mixture can also be applied to sheets of material. It obviates the necessity for guard rings, and from an educational point of view it brings into prominence the fact that the dielectric constant is primarily a Volume constant of matter.

LV. *On the Flow of Liquids into Capillary Tubes.* By C. H. BOSANQUET, M.A., *Lee's Reader in Physics, Christ Church, Oxford* *.

THE equations of motion of a liquid flowing into a capillary tube under the influence of its surface tension and of a hydrostatic pressure have been examined in some detail by Washburn (Phys. Rev. xvii. p. 273, 1921). He obtains a formula giving the time taken by the meniscus to pass between two points in a straight uniform capillary inclined at any angle to the vertical.

In his treatment, forces due to changes of the momentum of the liquid column are neglected, and the object of the present paper is to examine the effects due to these forces, and determine under what circumstances they become inappreciable.

* Communicated by the Author.

The simplest case, which is capable of a rigorous solution if Poiseuille's law be assumed to hold, is that of a liquid flowing from a reservoir of large area into an evacuated horizontal capillary.

If P is the pressure at the entrance to the capillary, and the other symbols have the usual significance, then the accelerating force is $P\pi r^2 + 2\pi rT$, the viscous retarding force is $8\pi\eta r\dot{x}$ and the momentum of the liquid column $\pi r^2\rho x\dot{x}$.

The equation of motion thus becomes:—

$$\frac{d}{dt}(\pi r^2\rho x\dot{x}) + 8\pi\eta r\dot{x} = P\pi r^2 + 2\pi rT.$$

Let
$$\frac{8\eta}{r^2\rho} = a, \quad \frac{Pr + 2T}{r\rho} = b.$$

Then
$$\frac{d}{dt}x\dot{x} + ax\dot{x} = b,$$

$$x\dot{x} = \frac{b}{a}(1 - e^{-at}) = \frac{1}{2} \cdot \frac{d}{dt}x^2.$$

$$\therefore x_2^2 - x_1^2 = \frac{2b}{a} \left\{ t - \frac{1}{a}(1 - e^{-at}) \right\}. \quad . \quad . \quad . \quad (1)$$

This case was treated by Rideal in a recent paper (Phil. Mag. Dec. 1922, p. 1152) with rather different results. He writes his differential equation

$$x\ddot{x} + ax\dot{x} = b,$$

omitting a term in $(\dot{x})^2$ which represents the force required to impart momentum to the liquid entering the tube. As the result of this omission he obtains a different expression, which he gives as

$$t = \frac{a}{2b}x^2 - \frac{1}{a}\log x + \dots$$

From this he concludes that x is a linear function of $\sqrt{t}$ if x is neither very small nor very large, and his curves appear to be plotted on the assumption that

$$x_2 - x_1 = \sqrt{\frac{2bt}{a}} + \text{a constant}$$

as soon as a state of steady motion has been attained.

Owing to the fact that in his experiments x_1 was fairly small, he obtains a linear relation within the error of experiment for values of $x_2 > 2x_1$, but the values of $\frac{T}{\eta}$ deduced

from the slope of the curves must be subject to a systematic error of six or seven per cent.

Equation (1) above reduces to that of Washburn if r is very small or if the meniscus is not timed from rest, but allowed to attain a state of steady motion before taking any readings.

In the case of ether in a capillary of 1 mm. diameter a has the value 10 sec^{-1} at about 20° , so that $\frac{1}{a}$ is negligible for tubes of smaller diameter. $a > 10$ for almost all other liquids in a 1 mm. capillary.

If the capillary has a total length l and initially contains a gas of viscosity η' and density ρ' , the viscous resistance becomes $8\pi\dot{x}\{\eta x + \eta'(l-x)\}$, and the momentum of the contents of the tube $\pi r^2\dot{x}\{\rho x + \rho'(l-x)\}$.

$$\text{Let } \frac{l\eta'}{\eta - \eta'} = x_\eta, \quad \frac{l\rho'}{\rho - \rho'} = x_\rho;$$

then

$$\frac{d}{dt}(x + x_\rho)(\rho - \rho')\dot{x} + \frac{8}{r^2}(x + x_\eta)(\eta - \eta')\dot{x} = P + \frac{2T}{r},$$

$$\text{if } (x + x_\eta) = \xi, \quad (x_\eta - x_\rho) = \xi_0,$$

$$\text{then } \frac{d}{dt}(\xi - \xi_0)\dot{\xi} + \alpha\xi\dot{\xi} = \beta. \quad \dots \dots (2)$$

As a first approximation $\dot{\xi} = \frac{\beta}{\alpha\xi}$ after the initial period of acceleration, so that

$$\frac{d}{dt}(\xi - \xi_0)\dot{\xi} = \frac{\beta^2\xi_0}{\alpha^2\xi^3},$$

Using this result,

$$\alpha\xi\dot{\xi} = \beta - \frac{\beta^2\xi_0}{\alpha^2\xi^3}.$$

Proceeding in this way by successive approximations a value of $\dot{\xi}$ is obtained which is less than $\frac{\beta}{\alpha\xi}$ if $x_\eta > x_\rho$,

$$t = \int \frac{d\xi}{\dot{\xi}},$$

$$\begin{aligned} \frac{1}{\dot{\xi}} = & \frac{\alpha\xi}{\beta} + \frac{\xi_0}{\alpha\xi^2} + \frac{3\beta\xi_0}{\alpha^3\xi^4} - \frac{4\beta\xi_0^2}{\alpha^4\xi^5} + \frac{15\beta^2\xi_0}{\alpha^5\xi^6} \\ & - \frac{48\beta^2\xi_0^2}{\alpha^6\xi^7} + \frac{35\beta^2\xi_0^3}{\alpha^6\xi^8} + \dots \end{aligned}$$

Then if the steady state has been attained by the time $\xi = \xi_1$

and ξ_2 is very large,

$$t = \frac{\alpha}{2\beta} (\xi_2^2 - \xi_1^2) + \frac{1}{\alpha} \cdot \frac{\xi_0}{\xi_1} \left\{ 1 + \frac{\beta}{\alpha^2 \xi_1^2} \left(1 - \frac{\xi_0}{\xi_1} \right) + \frac{\beta^2}{\alpha^4 \xi_1^4} \left(3 - 8 \frac{\xi_0}{\xi_1} + 5 \frac{\xi_0^2}{\xi_1^2} \right) + \dots \right\},$$

or

$$t = \frac{\alpha}{2\beta} (\xi_2^2 - \xi_1^2) + \frac{1}{\alpha} \phi(\xi_1). \quad \dots \quad (3)$$

If the density of the gas is negligible and the liquid starts from the end of the tube $\xi_1 = \xi_0$ and $\phi(\xi_1) = 1$,

$$t = \frac{\alpha}{2\beta} (\xi_2^2 - \xi_0^2) + \frac{1}{\alpha} (1 - \phi(\xi_2)). \quad \dots \quad (4)$$

In this case the steady state is attained instantaneously so that no time is lost in accelerating.

If ξ_1 is large compared with ξ_0 , as a first approximation

$$\xi \ddot{\xi} = \frac{\beta}{\alpha} (1 - e^{-\alpha t}),$$

$$\xi_0 \ddot{\xi} = \frac{\xi_0}{\xi} \left(1 + \frac{\beta}{\alpha^2 \xi^2} \right) \frac{d}{dt} (\xi \dot{\xi}) - \frac{\beta^2}{\alpha^2 \xi^2} \cdot \frac{\xi_0}{\xi}.$$

Then from (2)

$$\frac{d}{dt} (\xi \dot{\xi}) = \beta - \alpha \xi \dot{\xi} + \xi_0 \ddot{\xi},$$

$$\therefore \frac{d}{dt} (\xi \dot{\xi}) = \frac{\beta \left(1 - \frac{\beta}{\alpha^2 \xi^2} \cdot \frac{\xi_0}{\xi} \right) - \alpha \xi \dot{\xi}}{1 - \frac{\xi_0}{\xi} \left(1 + \frac{\beta}{\alpha^2 \xi^2} \right)}.$$

If $\frac{1}{\xi}$ does not change appreciably while the liquid is accelerating,

$$\xi \dot{\xi} = \left(\frac{\beta}{\alpha} - \frac{\beta^2}{\alpha^2 \xi_1^2} \cdot \frac{\xi_0}{\xi_1} \right) \left(1 - e^{-\frac{\alpha t}{1 - \frac{\xi_0}{\xi_1} \left(1 + \frac{\beta}{\alpha^2 \xi_1^2} \right)}} \right)$$

to a first approximation,

and if ξ_2 is very large compared with ξ_0

$$\begin{aligned} t &= \frac{\alpha}{2\beta} (\xi_2^2 - \xi_1^2) + \frac{1}{\alpha} \cdot \frac{\xi_0}{\xi_1} \left(1 + \frac{4\beta}{\alpha^2 \xi_1^2} \cdot \frac{\xi_0}{\xi_1} + \dots \right) \\ &\quad + \frac{1}{\alpha} \left(1 - \frac{\xi_0}{\xi_1} \left(1 + \frac{\beta}{\alpha^2 \xi_1^2} \right) \right) \\ &= \frac{\alpha}{2\beta} (\xi_2^2 - \xi_1^2) + \frac{1}{\alpha} \left(1 - \frac{\xi_0}{\xi_1} \cdot \frac{\beta}{\alpha^2 \xi_1^2} \left(1 - \frac{4\xi_0}{\xi_1} \right) + \dots \right). \end{aligned}$$

If ξ_1 is large the last term is very small, also it disappears on continuing the approximation, so that if the steady state is reached before $\xi = \xi_2$

$$t = \frac{\alpha}{2\beta} (\xi_2^2 - \xi_1^2) + \frac{1}{\alpha} (1 - \phi(\xi_2)).$$

This is identical with (4).

In general

$$t = \frac{\alpha}{2\beta} (\xi_2^2 - \xi_1^2) + \frac{1}{\alpha} (1 - \phi(\xi_2)) - \frac{1}{\alpha} (1 - \phi(\xi_1)) e^{-\frac{\alpha t}{1 - \phi(\xi_1)}} + \dots \quad (5)$$

The subsequent terms in the exponential are terms in t^3 and higher powers of t .

Substituting for α, β, ξ ,

$$\begin{aligned} t + \frac{r^2(\rho - \rho')}{8(\eta - \eta')} (1 - \phi(x_1 + x_\eta)) e^{-8(\eta - \eta')t / r^2(\rho - \rho')(1 - \phi(x_1 + x_\eta))} \\ = \frac{4(\eta - \eta')}{2rT + r^2P} ((x_2 + x_\eta)^2 - (x_1 + x_\eta)^2) \\ + \frac{r^2(\rho - \rho')}{8(\eta - \eta')} (1 - \phi(x_2 + x_\eta)). \quad (6) \end{aligned}$$

This reduces to (1) if η' and ρ' are put equal to zero, and to Washburn's equation if the second term on each side of the equation is omitted.

If the capillary is inclined upwards at an angle θ to the horizontal then, if $\gamma = g \sin \theta$, $\beta = \frac{Pr + \gamma r \rho' + 2T}{r(\rho - \rho')}$, and $X = \frac{\beta}{\gamma} + \xi_0 - \xi$,

$$\frac{d}{dt} (\xi - \xi_0) \dot{\xi} + \alpha \xi \dot{\xi} = \beta - \gamma (\xi - \xi_0) = \gamma X.$$

As a first approximation $\xi \dot{\xi} = \frac{\gamma}{\alpha} X$,

$$\frac{d}{dt} (\xi - \xi_0) \dot{\xi} = \frac{\gamma}{\alpha} \left(1 - \frac{\xi_0}{\xi} - \frac{X \xi_0}{\xi^2} \right) \dot{X},$$

$$\frac{1}{\xi} = \frac{\alpha \xi}{\gamma X} - \frac{1}{\alpha X} + \frac{\xi_0}{\alpha X \xi} + \frac{\xi_0}{\alpha \xi^2},$$

Phil. Mag. S. 6. Vol. 45. No. 267. March 1923. 2 M

$$\begin{aligned}
&= \int_{X_2}^{X_1} \left(\frac{\alpha\beta}{\gamma^2 X} + \frac{\alpha\xi_0}{\gamma X} - \frac{\alpha}{\gamma} - \frac{1}{\alpha X} \right) dX \\
&\quad + \frac{\xi_0}{\alpha} \int_{\xi_1}^{\xi_2} \left(\frac{1}{\gamma \xi + \xi_0 \xi - \xi^2} + \frac{1}{\xi^2} \right) d\xi \\
&= \left(\frac{\alpha\beta}{\gamma^2} + \frac{\alpha\xi_0}{\gamma} - \frac{1}{\alpha} \right) \log \frac{\beta + \gamma\xi_0 - \gamma\xi_1}{\beta + \gamma\xi_0 - \gamma\xi_2} - \frac{\alpha}{\gamma} (\xi_2 - \xi_1) \\
&\quad + \frac{\xi_0}{\alpha} \left(\frac{1}{\xi_1} - \frac{1}{\xi_2} \right) + \frac{\gamma\xi_0}{\alpha(\beta + \gamma\xi_0)} \left(\log \frac{\beta + \gamma\xi_0 - \gamma\xi_1}{\beta + \gamma\xi_0 - \gamma\xi_2} - \log \frac{\xi_1 - \xi_0}{\xi_2 - \xi_0} \right) \dots \dots (7)
\end{aligned}$$

To this must be added a correction if the liquid starts from rest. The magnitude of the correction will be

$$\frac{1}{\alpha} \left(1 - \frac{\xi_0}{\xi_1} \right) \left(1 - e^{-\frac{\alpha\xi_1 t}{\xi_1 - \xi_0}} \right).$$

The time for a liquid starting from rest is thus given by :—

$$\begin{aligned}
&t + \frac{1}{\alpha} \left(1 - \frac{\xi_0}{\xi_1} \right) e^{-\frac{\alpha\xi_1 t}{\xi_1 - \xi_0}} \\
&= \left(\frac{\alpha\beta}{\gamma^2} + \frac{\alpha\xi_0}{\gamma} - \frac{1}{\alpha} + \frac{\gamma\xi_0}{\alpha(\beta + \gamma\xi_0)} \right) \log \frac{\beta + \gamma\xi_0 - \gamma\xi_1}{\beta + \gamma\xi_0 - \gamma\xi_2} \\
&\quad - \frac{\alpha}{\gamma} (\xi_2 - \xi_1) + \frac{1}{\alpha} \left(1 - \frac{\xi_0}{\xi_2} \right) + \frac{\gamma\xi_0}{\alpha(\beta + \gamma\xi_0)} \log \frac{\xi_2 - \xi_0}{\xi_1 - \xi_0}. \quad (8)
\end{aligned}$$

This reduces to (5) if γ is vanishingly small and $\phi(\xi) = \frac{\xi_0}{\xi}$, and if the terms in $\frac{1}{\alpha}$ are omitted it reduces to Washburn's equation. Developing the series as far as first order terms in γ the formula becomes :—

$$\begin{aligned}
&t + \frac{1}{\alpha} \left(1 - \frac{\xi_0}{\xi_1} \right) e^{-\frac{\alpha\xi_1 t}{\xi_1 - \xi_0}} \\
&= \frac{\alpha}{2\beta} (\xi_2^2 - \xi_1^2) + \frac{\alpha\gamma}{3\beta^2} (\xi_2^3 - \xi_1^3) - \frac{\gamma}{\alpha\beta} (\xi_2 - \xi_1) + \frac{1}{\alpha} \left(1 - \frac{\xi_0}{\xi_2} \right).
\end{aligned}$$

This form gives the effect due to a slight change of head with motion of the meniscus.

Observations of the rate of flow of a liquid into or out of a horizontal capillary under the influence of various initial values of P provide a method of determining both viscosity and surface tension. If t' is the value which the time would have if the density were zero, then

$$\frac{d\xi^2}{dt'} = \frac{r^2 P + 2rT}{4\eta},$$

and measurements with two values of P yield both the viscosity and the surface tension.

The dynamic method of measuring surface tension has certain advantages over the static method ; the mean radius of the tube is required instead of the radius at one point, also the surface is being continuously renewed, thus reducing the risk of contamination. The method is also adaptable to the measurement of interfacial surface tensions and to the comparison of angles of contact with an advancing or receding meniscus.

In conclusion I wish to thank Professor F. A. Lindemann, F.R.S., for the interest which he has taken in this work.

Summary.

(1) The motion of a liquid flowing into a horizontal evacuated capillary under the influence of a constant head is examined and an expression is obtained which is rigorous if Poiseuille's law holds.

(2) The equations are extended to the case of two fluids in contact and an approximate solution is obtained.

(3) Similar formulæ are deduced for the case of a liquid flowing into an inclined tube.

LVI. Temperature Measurement with the Einthoven Galvanometer. By F. ADCOCK, M.Sc., and E. H. WELLS, M.Sc., late Bowen Research Scholars in Mechanical Engineering*.

[Plates IX. & X.]

CONTENTS.

	Page
The Object of the Present Work	532
Description of the Apparatus	534
The Mathematical Theory of the Unbalanced Wheatstone's Bridge	538
Experimental Results	547
Conclusion	560

THE OBJECT OF THE PRESENT WORK.

THE Einthoven galvanometer (see Pl. IX. fig. 1) has been used by a number of investigators† for the purpose of determining temperatures in the gas-engine cylinder, and their work clearly shows the practicability of recording quantitative results for the cycle of temperature in the heat-engine cylinder.

In order that the results recorded may be interpreted as temperature of the gas itself, it is necessary to know the relationship between the true temperature and the temperature assumed by the thermometer. It is the object of this research to investigate this relationship.

The difference between the temperature assumed by the thermometer and the temperature of the gas at any instant, which may be termed the "temperature lag," will depend

* Communicated by Prof. F. W. Burstall, M.Sc., M.A., M.Inst.C.E., M.I.Mech.E.

† For a history of Temperature Measurement in the Internal Combustion Engine, see the following:—

Burstall: "On the Measurement of Cyclically Varying Temperature," *Phil. Mag.*, Sept. 1895.

B. Hopkinson: "On the Measurement of Gas Engine Temperatures," *Phil. Mag.*, 1907.

Callendar and Dalby: "On the Measurement of Temperatures in the Cylinder of a Gas Engine," *Proc. R. S.*, A lxx., 1908.

Coker and Scoble: *Proc. Inst. C.E.* vol. xcvi., Part II., 1913-14.

Petersen: *Verfahren zur Messung Schnell Wechselnder Temperaturen*, 1913.

Nagel: *Zeitschrift des Vereins Deutscher Ingenieure*, 5th July, 1913.

E. B. Wolff: *Temperatuurmetingen in een Dieselmotor*, 1913.

mainly on the following points, the effects of which require investigation :—

- (1) The form of the thermometer employed.
- (2) The rate of variation of temperature of the gas.
- (3) The nature and temperature of the walls of the containing vessel.
- (4) The velocity of gas relative to the thermometer.

It is intended that the thermometer which will be employed in the gas engine shall be of the type used in Professor Burstall's earlier work, *i. e.* the platinum resistance thermometer. The investigation, therefore, refers primarily to the platinum resistance thermometer, and apparatus has been designed and constructed accordingly.

The scheme adopted consists of maintaining steady temperatures of different intensity in different regions and moving the thermometer through these regions to obtain the cyclical variation of temperature ; the rate of variation of temperature is determined by the frequency of movement of the thermometer through the different temperature regions, and this can be varied within wide limits.

To study the effect of point (3), different methods of heating and cooling in the respective regions must be employed. The first type of apparatus embodies a vertical silica tube of which the upper part is wound with an electrical resistance heater, and the lower part is enclosed in a box through which water can be circulated. The thermometer can be reciprocated axially in the interior of the silica tube. Precautions are taken to reduce motion of the air in the tube to the minimum, and the natural convection tends to the same end ; but it is clear that the heating of the thermometer is largely by radiation from the walls of the silica tube.

Further work will be necessary to determine the effect of conditions such as those obtaining in the gas-engine cylinder, *viz.* cold walls and hot gas. These conditions would be approximated in an apparatus wherein a current of heated air and a current of air at atmospheric temperature pass along adjacent channels, the walls of which are water-jacketed. The thermometer would reciprocate between the two channels.

The effect of varying the velocity of gas relative to the thermometer may be studied in the apparatus under consideration by varying the frequency of reciprocation of the thermometer, and, to avoid changing the rate of variation of

the temperature at the same time, the limits of temperature may be varied as necessary.

In the design of the experimental thermometer it was necessary to provide for the fulfillment of the following conditions as closely as possible.

The carrying device must be light in weight so that the inertia when moving the thermometer at considerable speeds should not be excessive.

The air through which the thermometer moves should be disturbed as little as possible by the reciprocation of the thermometer.

Conditions favouring the formation of a pocket of air round the thermometer and carried with it must be avoided.

The temperature throughout the path of the thermometer travel must be known, and means must be provided for independent measurement of this while the thermometer is reciprocating.

The whole of the thermometer must be in a region of uniform temperature at any instant, and the compensating leads must be at the same temperature as the main leads at any corresponding part of their length.

DESCRIPTION OF THE APPARATUS.

A silica tube (1) (see fig. 2 and Pl. X. fig. 3), of two inches internal diameter and twelve inches long, is mounted vertically between two hard asbestos sheets (2), which are bolted to brackets on the main framework. The upper part of the silica tube is wound with a resistance coil (3) embedded in Alundum cement, and lagged with non-conducting material (4).

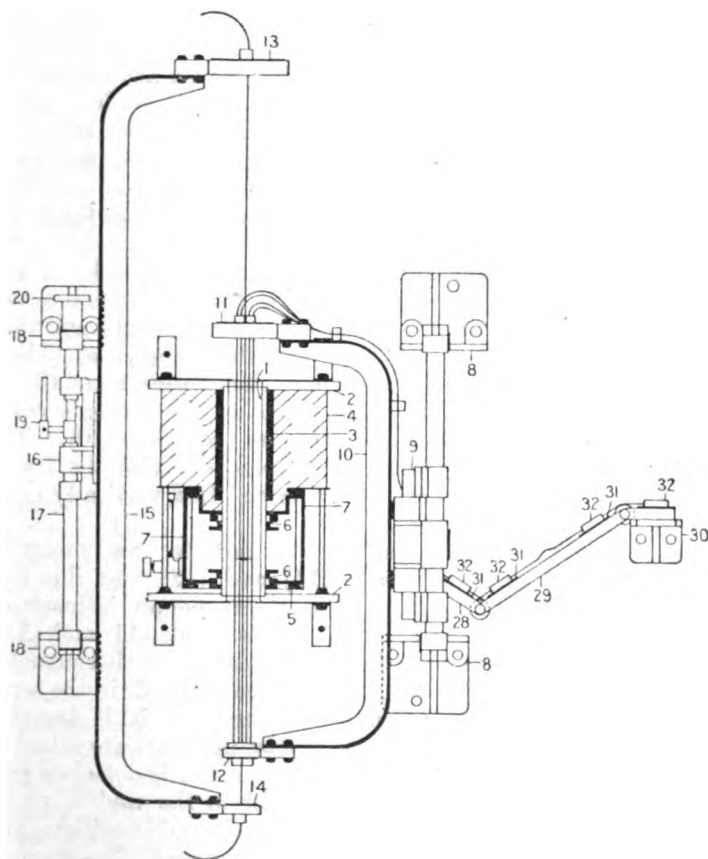
The lower part of the silica tube is enclosed by a water vessel (5) which has glands (6) packed with asbestos. Access to the glands is obtained by removing the sides of the water vessel (7). Provision is made so that water may be circulated through the vessel, the overflow being near the top.

The brackets (8) carry slide-bars on which the cross-head (9) reciprocates. A pointer and scale are provided to indicate the position of the cross-head with respect to the main frame and the stroke length. The frame (10) is bolted to the cross-head and carries the insulating heads (11) and (12). Between pairs of terminals on the insulating heads (11) and (12) run four carrying wires through the interior of the silica tube. The thermometer wire spans two of the carrying

wires and two more are bridged to form a compensating circuit.

The carrying wires are placed in such positions that the fine thermometer wire is about one inch long and the fine wire in the compensator circuit about half an inch long.

Fig. 2.



Sectional Elevation of Apparatus.

Short pieces, about 0.1 in. long, of platinum wire, 0.01 in. diameter, are silver soldered to the carrying wires and the fine platinum wire in each circuit is gold soldered to these short pieces. The two circuits are made exactly similar except for the difference in length of the fine platinum wire. This difference is the length of platinum wire in the ideal

resistance thermometer to which the experimental thermometer corresponds. The platinum wires in the two circuits lie in one plane normal to the axis of the silica tube so that they shall be as nearly as possible at the same temperature.

Between the fine wires in the thermometer and compensator circuits, a fine wire thermocouple is carried inside the silica tube by the insulating heads (13) and (14) attached to the frame (15). This is capable of independent movement parallel to the motion of the thermometer by movement of the slider (16) on the slide-bars (17), which are carried by brackets (18) on the main framework. This slider can be clamped at any part of its travel by a clamping bolt (19), and small movements can be effected by rotating the knob (20). A pointer attached to the slider registers positions of the thermocouple by means of a scale fixed to the main framework.

The procedure in mounting the thermometer and thermocouple is as follows:—A steel rod is passed through a hole provided in the head (11) and into the silica tube and then screwed into the head (12), after which the head (11) is secured to the rod. The steel rod thus forms an auxiliary frame by means of which, after releasing the fixing screws, the insulating heads are removed from the frame (10). The upper thermocouple head (13) is removed from the frame (15) to allow the auxiliary frame to be lifted vertically clear of the apparatus.

The carrying wires for the thermometer are mounted between the insulating heads (11) and (12) and the fine wires are soldered to them. The thermocouple is mounted up, being temporarily attached to the heads (11) and (12). The thermojunction and the fine wires of the thermometer and compensator circuits are arranged to be all in the same plane. When this assembly is complete it is inserted through the silica tube and the insulating heads are attached to the frame (10), after which the steel rod is detached and removed. The cross-head is brought to the middle of its stroke and the thermocouple slider to its mid-position, and the readings on the respective scales are noted. The thermocouple is attached to the insulating heads (13) and (14) and then released from the thermometer assembly. The thermocouple can be brought to any desired point in the stroke of the thermometer by reference to the two initial readings.

The thermometer may at any time be removed from the apparatus for inspection by inserting the steel rod and fixing to it the heads (11) and (12) and releasing them from the frame (10); but the thermocouple must first be clamped to these heads and released from its insulating heads (13) and (14).

The cross-head (9) of the thermometer frame is actuated through a connecting-rod by a crank pin on the crank disk (see Pl. X. fig. 3). The crank disk functions as a flywheel, giving a small coefficient of irregularity of angular velocity at high speed. Balance weights are formed integral with the crank disk so that a static balance of the reciprocating parts is obtained, giving a small coefficient of irregularity of angular velocity at slow speeds.

The crank disk is carried on a shaft running in the two bearings of a pedestal and the shaft is driven by a pulley. A similar pedestal is mounted on the framework and carries a countershaft. A flat leather belt runs on a pulley on the countershaft and the pulley on the main shaft, giving a speed reduction of four to one. An electric motor which runs at maximum speed of 1350 r.p.m. drives the apparatus by a cotton driving-rope running over a pair of grooved pulleys having five steps, giving a series of speeds which form an arithmetic progression. One cone pulley is keyed to the countershaft and the other is carried on the motor shaft. After a number of experiments had been carried out, another shaft with a pair of pulleys was introduced between the countershaft shown in Pl. X. fig. 3 and the main shaft in order to give further reduction in speed.

Speed regulation of the motor is obtained by means of a rheostat in the armature circuit which can be connected either as a potentiometer or as a series resistance.

Four leads from the insulating head (11) to some fixed part of the apparatus are required to connect the thermometer and compensating circuits to the bridge. It is of great importance that the resistance of these leads should be unaffected by the reciprocation, so that sliding contacts cannot be used. Two swinging links (28) and (29) connect the cross-head to a bracket (30) on the main framework. Insulating blocks (31) are screwed to the cross-head, the two swinging links, and the bracket; and groups of four terminals (32) are attached to each insulating block.

Coiled around the axis pin of each moving joint, a helix of springy brass wire connects each corresponding pair of terminals. Movement of the cross-head produces flexion in the wire of the helix, but the strain is kept low and no change in resistance can be detected. From the terminals on the fixed bracket (30) stout leads are taken to the Wheatstone's bridge.

In order to register the temperature readings on the photographic plate with respect to the position of the thermometer in its stroke, a small pointer was attached to the

armature of an electromagnet which was mounted on the front of the camera. The electric circuit through this magnet was completed by a contact made at the top and bottom of the stroke, thus producing a continuous line on the plate with a small kick each time the current was allowed to pass. For this idea the authors are indebted to Dr. E. B. Wolff (Temperatuurmetingen in een Dieselmotor, 1913).

THE MATHEMATICAL THEORY OF THE UNBALANCED WHEATSTONE'S BRIDGE.

In fig. 4, let P , Q , R , and S be the resistance of the four arms of the bridge, and G the resistance of the galvanometer. Let e be the potential difference across the bridge

Fig. 4.

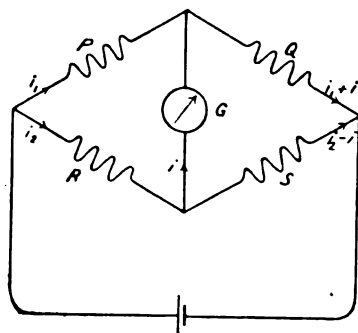


Diagram of Wheatstone's Bridge.

and r the potential difference across the galvanometer. Let i_1 be the current in P , i_2 the current in R , and i the current in the galvanometer.

The current in Q will be $i_1 + i$.

The current in S will be $i_2 - i$.

The potential difference across P will be $i_1 P$.

The potential difference across Q will be $(i_1 + i) Q$.

The potential difference across R will be $i_2 R$.

The potential difference across S will be $(i_2 - i) S$.

The potential difference across G will be $i G$.

The three currents i_1 , i_2 , and i are connected by the following three equations:—

$$\text{Sum of p.d.'s across } P \text{ and } Q, \quad i_1 P + (i_1 + i) Q = e. \quad (1)$$

$$\text{Sum of p.d.'s across } R \text{ and } S, \quad i_2 R + (i_2 - i) S = e. \quad (2)$$

$$\text{Dif. of p.d.'s across } P \text{ and } R, \quad i_1 P - i_2 R = r = i G. \quad (3)$$

These three equations are now to be solved.

From (1) and (3),

$$i_1 P + \left(i_1 + \frac{i_1 P - i_2 R}{G} \right) Q = e. \quad (4)$$

From (2) and (3),

$$i_2 R + \left(i_2 - \frac{i_1 P - i_2 R}{G} \right) S = e. \quad (5)$$

From (4),

$$\begin{aligned} i_1 P G + i_1 G Q - i_2 R Q + i_1 P Q &= e G, \\ i_1 (P G + G Q + P Q) - i_2 R Q &= e G. \end{aligned} \quad (6)$$

From (5),

$$\begin{aligned} i_2 R G + i_2 G S + i_2 R S - i_1 P S &= e G, \\ i_2 (R G + G S + R S) - i_1 P S &= e G. \end{aligned} \quad (7)$$

From (6),

$$i_1 (P^2 S G + P Q S G + P^2 Q S) - i_2 P Q R S = e P S G. \quad (8)$$

From (7),

$$\begin{aligned} -i_1 (P^2 S G + P Q S G + P^2 Q S) + i_2 (P R G^2 + Q R G^2 + P Q R G \\ + P S G^2 + Q S G^2 + P Q S G + P R S G + Q R S G + P Q R S) \\ = e G^2 P + e G^2 Q + e G P Q. \end{aligned} \quad (9)$$

From (8) and (9),

$$\begin{aligned} i_2 (P R G^2 + Q R G^2 + P Q R G + P S G^2 + Q S G^2 + P Q S G \\ + P R S G + Q R S G) = e P S G + e G^2 P + e G^2 Q + e G P Q, \\ i_2 = e \frac{P S + G P + G Q + P Q}{P R G + Q R G + P Q R + P S G + Q S G + P Q S} \cdot \left. \begin{aligned} &+ P R S + Q R S \end{aligned} \right\} \quad (10)$$

From (7) and (10),

$$\begin{aligned} i_1 P S &= e \left(\frac{(R G + G S + R S) (P S + G P + G Q + P Q)}{P R G + Q R G + P Q R + P S G + Q S G} - G \right) \\ &\quad + P Q S + P R S + Q R S \\ &= e \left(\frac{2 P R S G + P R G^2 + Q R G^2 + P Q R G + P G S^2 + P S G^2}{P R G + Q R G + P Q R + P S G + Q S G + P Q S} - G \right) \\ &\quad + P R S + Q R S \\ &= e \frac{P Q R S + P R S G + P G S^2 + P R S^2}{P R G + Q R G + P Q R + P S G + Q S G + P Q S} \\ &\quad + P R S + Q R S \\ i_1 &= e \frac{Q R + R G + G S + R S}{P R G + Q R G + P Q R + P S G + Q S G + P Q S} \cdot \left. \begin{aligned} &+ P R S + Q R S \end{aligned} \right\} \quad (11) \end{aligned}$$

From (10), (11), and (3),

$$\begin{aligned}
 v = iG &= e \frac{-QRG - PQR + PQR + RPG + PSG + PRS - PRS - PRG}{PRG + QRG + PQR + PSG + QSG + PQS + PRS + QRS} \\
 &= e \frac{PSG - QRG}{PRG + QRG + PQR + PSG + QSG + PQS + PRS + QRS} \quad (12)
 \end{aligned}$$

$$i = e \frac{PS - QR}{RPG + QRG + PQR + PSG + QSG + PQS + PRS + QRS} \quad (13)$$

Application to Resistance Thermometer.

In the ordinary form of resistance thermometer, a resistance wire is inserted in the arm P of the bridge, and a pair of compensating leads is inserted in the arm Q to neutralize the effect of change in resistance of the main leads. In order that the compensation shall be accurate it is necessary that the resistance S bear to R the same ratio as the resistance of the compensating leads bears to the resistance of the main leads, and the balance obtained by adding extra resistance to the Q arm. It is convenient to make the compensating leads exactly similar to the main leads and this necessitates R and S being equal. When a balance is obtained, therefore, $P = Q$. When a balance is not obtained, the p.d. across the galvanometer is given, from equation (12), by

$$\begin{aligned}
 v &= e \frac{(P - Q)G}{(P + Q)(2G + R) + 2PQ} \\
 &= e \frac{P - Q}{\left(2 + \frac{R}{G}\right)(P + Q) + \frac{2}{G}PQ} \quad (14)
 \end{aligned}$$

This method of connecting up the Wheatstone's bridge may be termed a "series" arrangement, since the thermometer and compensating circuits are in series with respect to the battery current. If we interchange the battery and galvanometer we obtain what may be termed a "parallel" arrangement, since the thermometer and compensating circuits will now be in parallel with respect to the battery

current. This method of connecting up will now be considered. The most convenient way to do this is to interchange P and S in equation (12). This gives

$$v = e \frac{\text{SPG} - \text{QRG}}{\text{SRG} + \text{QRG} + \text{SQR} + \text{SPG} + \text{QPG} + \text{SQP} + \text{SRP} + \text{QRP}}$$

Putting S = R,

$$\begin{aligned} v &= e \frac{\text{RPG} - \text{QRG}}{\text{R}^2\text{G} + \text{QRG} + \text{R}^2\text{Q} + \text{RPG} + \text{QPG} + \text{RQP} + \text{R}^2\text{P} + \text{QRP}} \\ &= e \frac{(\text{P} - \text{Q})\text{RG}}{\text{R}^2(\text{P} + \text{Q} + \text{G}) + \text{RG}(\text{P} + \text{Q}) + \text{PQ}(2\text{R} + \text{G})} \\ &= e \frac{(\text{P} - \text{Q})\text{RG}}{(\text{P} + \text{Q})(\text{R}^2 + \text{RG}) + \text{R}^2\text{G} + \text{PQ}(2\text{R} + \text{G})} \\ &= e \frac{\text{P} - \text{Q}}{\left(1 + \frac{\text{R}}{\text{G}}\right)(\text{P} + \text{Q}) + \text{R} + \left(\frac{2}{\text{G}} + \frac{1}{\text{R}}\right)\text{PQ}} \quad \dots (15) \end{aligned}$$

The Relative Advantages of "Series" and "Parallel" Arrangements.

In the resistance thermometer as generally used, for example, in the Callendar Temperature Recorder, a slide wire is inserted between P and Q, and a connexion is made by means of a jockey at a balance point. Under these circumstances it is considered preferable that the sliding contact should not carry the main current, so the "series" arrangement is adopted, whereby the jockey only carries the galvanometer current, which is of necessity always small, and which vanishes when a balance is obtained.

For measuring cyclically varying temperatures, however, the slide wire is not necessary and other matters exert their claim for consideration, namely, the battery heating of the thermometer wire and the efficacy of the compensating circuit.

542 Messrs. F. Adcock and E. H. Wells on *Temperature
Battery Heating.*

Prof. G. Forbes gives for bare overhead wires :—

$$\text{Current} = \sqrt{\frac{d^3 t}{320 R}},$$

where d = diameter of wire in cms.

t = difference in temperature between wire and air in ° C.

and R = specific resistance of wire at limiting temperature in ohms per cm. cube.

According to this formula, if the specific resistance of platinum be assumed to be 44×10^{-6} ohm per cm. cube at 1000° C., and the temperature difference be limited to 5° C., the current in the thermometer wire will be as follows :—

Dia. of thermometer wire.	Current.
inches.	amperes.
·01	·0764
·00585	·0342
·0032	·0138
·0025	·00958
·002	·00685
·0015	·00445
·001	·00242

In all the theoretical calculations, this is assumed to be the maximum safe current, and this forms the basis of the comparison between the different arrangements and between different values of the resistances R and G in equations (14) and (15).

If this current be constant, as it will be very nearly if the platinum resistance forms only a small part of the resistance of the whole circuit, the temperature difference when the platinum is at 0° C. (taking the specific resistance as 11×10^{-6} ohm per cm. cube) is found by the same formula to be 1·25° C.

Thus, if this value be adopted, the heating of the platinum due to battery current is quite negligible.

Compensation.

It will be noticed that in both equations (14) and (15) the expressions $(P + Q)$ and PQ occur in the denominator,

consequently any increase in resistance which affects P and Q equally reduces the p.d. across the galvanometer—in other words, the compensators do not compensate except when a balance is obtained. This is a serious matter when using the Wheatstone's bridge for measuring cyclically varying temperatures, and its effect will now be considered.

It can be proved that when R is greater than P the parallel arrangement gives greater sensitivity and better compensation than the series, and that when R is less than P the series arrangement gives greater sensitivity and better compensation than the parallel.

This is best illustrated by taking an actual case. The expressions for v in equations (14) and (15) involve five quantities, e , R, G, P, and Q. Of these, P and Q, only, vary with the temperature of the thermometer; the remainder can have any values assigned to them, but, when once decided upon, remain constant throughout the experiment.

The method adopted for treating the problem mathematically is to obtain a balance when the thermometer is at 0°C . and calculate the p.d. across the galvanometer produced when the thermometer is at 1000°C . This is done for various values of e , R, and G, and for the series and parallel arrangements.

These results are plotted in figs. 5 and 6 for an experimental thermometer the particulars of which are as follows:—

Dia. of thermometer wire $\cdot 0032$ inch.

P circuit includes platinum the resistance of which at 0°C . is $\cdot 51$ ohm.

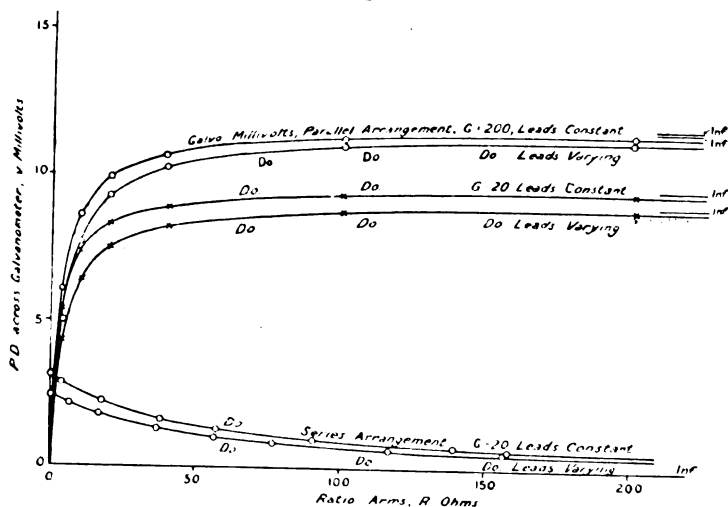
Q circuit includes platinum the resistance of which at 0°C . is $\cdot 22$ ohm.

Q circuit includes external resistance of $\cdot 29$ ohm in order to obtain a balance at 0°C .

Each circuit includes leads the resistance of which at 0°C . is $\cdot 88$ ohm.

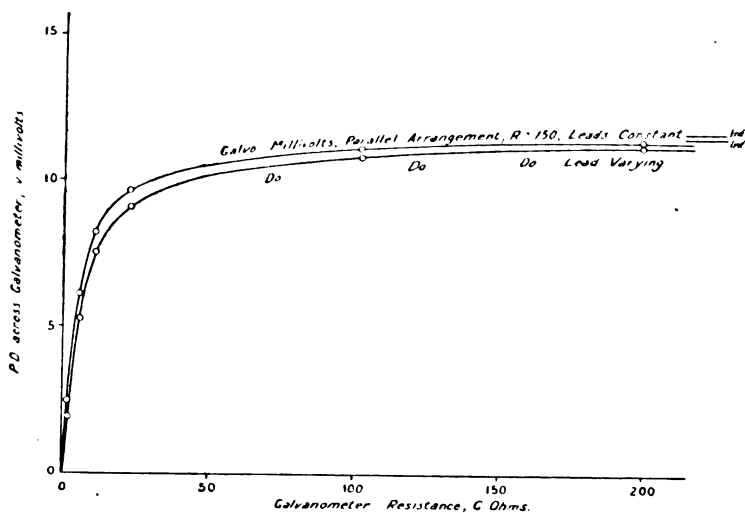
In order to find the effect of a change in resistance in leads, the resistance of the leads is assumed to increase by $\cdot 66$ ohm for the curves marked "leads varying." This increase in resistance would be occasioned by a length of 3 inches of the steel carrying wires, with which the experimental thermometer was originally mounted up, assuming the same temperature as the platinum.

Fig. 5.



Curve showing v against R .

Fig. 6.



Curve showing v against G .

Tables showing Error due to Heating of Carrying Wires.

Series Arrangement, G=20 ohms.		Parallel Arrangement, G=20 ohms.	
R ohms.	Error per cent.	R ohms.	Error per cent.
0	22.4	0	—
10	22.1	1	27.2
20	21.9	4	19.9
30	21.8	10	13.5
40	21.7	20	9.4
50	21.6	40	7.3
60	21.5	100	6.0
80	21.4	200	5.5
100	21.3	inf.	4.9
150	21.2		
200	21.1		
inf.	20.9		

Tables showing Error due to Heating of Carrying Wires.

Parallel Arrangement, G=200 ohms.		Parallel Arrangement, R=150 ohms.	
R ohms.	Error per cent.	G ohms.	Error per cent.
0	—	0	—
1	29.8	1	18.5
4	18.1	5	13.0
10	10.5	10	8.7
20	6.4	20	5.7
40	3.7	100	2.2
100	2.2	200	1.5
200	1.7	1000	1.04
inf.	.85	4000	.97
		inf.	.93

From calculations and these curves (figs. 5 and 6), the following deductions have been drawn :—

1. If R is greater than P, the parallel arrangement requires a higher e.m.f. than the series.
2. If R is greater than P, the parallel arrangement gives a greater sensitivity than the series.

Phil. Mag. S. 6. Vol. 45. No. 267. March 1923. 2 N

3. If R is greater than P, the parallel arrangement gives better compensation than the series.
4. With the series arrangement, greater sensitivity is obtained with a small value for R.
5. With the parallel arrangement, greater sensitivity is obtained with a large value for R, but very little is gained by increasing R beyond 150 ohms.
6. With the series arrangement, better compensation is obtained with a large value for R, but the improvement is small.
7. With the parallel arrangement, better compensation is obtained with a large value for R, but very little is gained by increasing R beyond 150 ohms.
8. For fibres which give the same deflexion per millivolt, greater sensitivity and better compensation are obtained with a high resistance fibre, but in neither case is there much to be gained by increasing G beyond 200 ohms.

The fibres supplied for use in the galvanometer had a resistance of the order of 20 ohms ; the curves have, therefore, been drawn for this value and also for 200 ohms.

In view of these deductions, it was decided to adopt the parallel arrangement, and make R equal to 150 ohms. This value has the advantage of requiring an e.m.f. which is very conveniently obtained, namely, 2·09 volts, or the e.m.f. of one accumulator cell.

For other diameters of thermometer wire and a 20-ohm fibre the corresponding values are as follows :—

Diameter. ins.	R ohms.	e volts.	v for 1000° C. volts.
·01	50	4	·0058
·00585	150	4	·0060
·0032	150	2	·0094
·0025	200	2	·0097
·002	300	2	·0098
·0015	400	2	·0094
·001	800	2	·0076

In view of the fact that the compensation is not exact when the bridge is unbalanced, it is important that the carrying wires should change their resistance by as small an amount as possible. After some trials copper was selected

as the most suitable material for two reasons: first, because its specific resistance is so low that any change in resistance is small compared with the platinum resistance, and, secondly, because its thermo e.m.f. with platinum is very small. The error due to heating of copper carrying wires is .85 per cent. against 5.7 per cent. for the stainless steel under the conditions adopted for the experiments.

The extent of the variation in the resistance of the leads and carrying wires can be halved by adopting the Siemens three-lead arrangement. As the variation in the resistance of the common lead will in general be negligible compared with the ratio-arms, the error due to heating of the carrying wires will consequently also be about halved.

The reason why the three-lead arrangement was not adopted in the present experiments was because it was thought desirable to make the thermocouple and resistance thermometer as symmetrical as possible, and a three-lead resistance thermometer would have been difficult to arrange symmetrically with respect to the thermocouple.

This objection would not hold in the case of a thermometer intended for use in a gas engine or in a gas engine type of apparatus, and it is therefore suggested that if experiments are carried out in a gas engine or gas engine type of apparatus the three-lead arrangement should be adopted.

EXPERIMENTAL RESULTS.

The procedure in making a set of tests was as follows. The resistance thermometer was set at the bottom of its stroke, that is in the cold part of the furnace tube, and the external resistance in the Q circuit was adjusted till an approximate balance was obtained, using the millivoltmeter in the bridge to avoid damaging the Einthoven fibre.

The Einthoven galvanometer was then connected to the bridge in place of the millivoltmeter and the latter was connected to the thermocouple.

By means of the scales provided for the purpose, the silica tube was explored with the resistance thermometer and thermocouple side by side. This provided both the stationary temperature distribution and the calibration of the resistance thermometer.

The resistance thermometer was then reciprocated by the motor and the speed counted by means of a stop-watch.

A loaded dark slide was inserted in the camera and the dashpot controlling the speed of fall of the plate carrier was adjusted so that between one and two cycles appeared on the plate.

After opening the dark slide the battery key was depressed and the plate allowed to fall, recording the galvanometer deflexion.

By means of a special stop having three steps the plate was brought to rest a short distance before the end of the plate had passed the slit. The battery key was released and the plate allowed to fall until the second step of the stop came into action, giving the zero position of the fibre. The motor was then shut down and the resistance thermometer set at the bottom of its stroke. With the battery key depressed the plate was allowed to fall until the third step of the stop came into action, giving the lower limit of temperature. The resistance thermometer was then moved to the top of its stroke, the battery key depressed, and the plate allowed to complete its fall, giving the upper limit of temperature. The battery key was released, the dark slide closed and taken out of the camera for development.

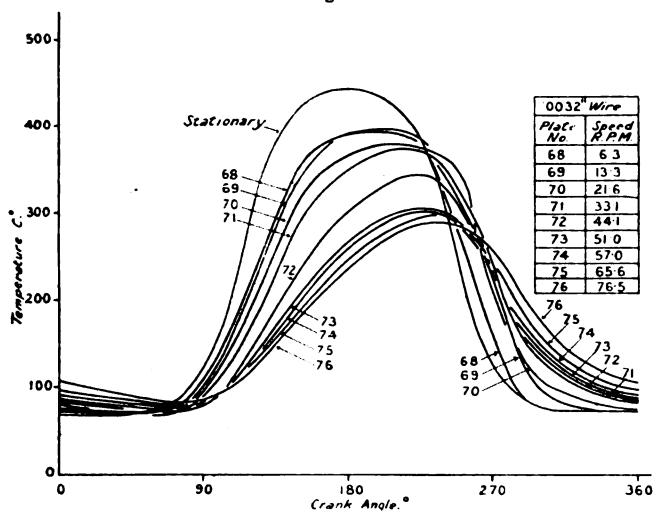
Thus each record consists of a wave and three discontinuous straight lines. The object of the zero position is obvious. The temperature limits are required to check variations in the voltage of the mains, and to correct the sensitivity accordingly.

Prints were taken from the plates and the interval between successive dead centres as indicated by the pointer in front of the camera was divided into intervals of 20 degrees of angle. The ordinates corresponding to these abscissæ were read and by reference to the calibration curve translated into temperatures.

Then all the curves corresponding to one set of tests, including the stationary temperature distribution, were plotted on the same crank angle base.

Figs. 7-15 show these resultant diagrams. The greatest discrepancy between the curve taken at speed and the stationary temperature distribution curve occurs at the upper dead centre. This is termed the temperature lag and is taken as a measure of the ability of the thermometer to follow the temperature changes.

Fig. 7.



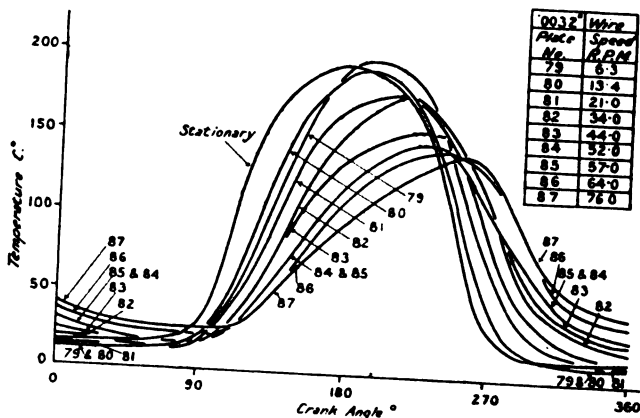
Experimental Curves, .0032 in. measuring wire.

.0032 in. Wire.

Temperature Range 370° C.

Plate No.	Lag. ° C.	Lag Range	Speed. r.p.m.
68	55.1	.15	6.3
69	51	.14	13.3
70	78.5	.21	21.6
71	92	.25	33.1
72	139	.38	44.1
73	176	.48	51.0
74	185	.50	57.0
75	197	.53	65.6
76	205	.56	76.5

Fig. 9



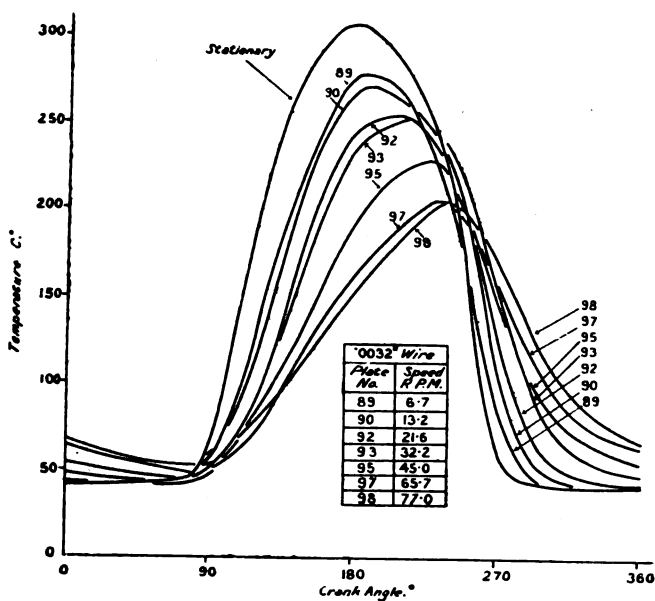
Experimental Curves, .0032 in. measuring wire.

.0032 in. Wire.

Temperature Range 180° C.

Plate. No.	Lag. ° C.	Lag Range	Speed. r.p.m.
79	2.5	.01	6.3
80	6	.03	13.4
81	30	.17	21
82	40	.22	34
83	60	.33	44
84	77.5	.43	52
85	77.5	.43	57
86	85	.47	64
87	100	.56	76

Fig. 9.



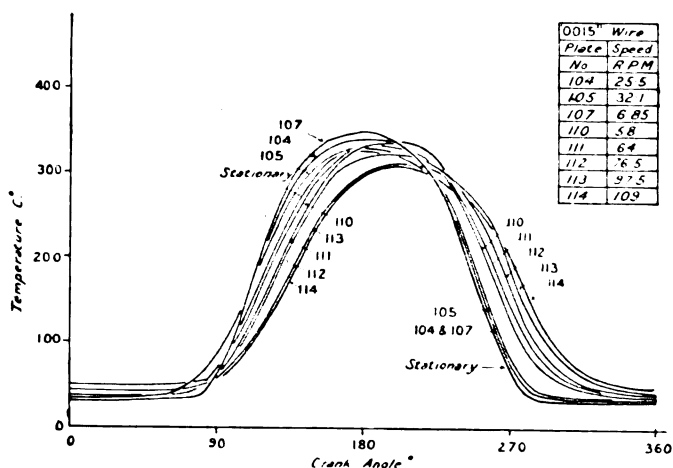
Experimental Curves, .0032 in. measuring wire.

.0032 in. Wire.

Temperature Range 260° C.

Plate No.	Lag. ° C.	Lag Range	Speed. r.p.m.
89	31	.12	6.7
90	40	.15	13.2
92	60	.23	21.6
93	75	.29	32.2
95	110	.42	45.0
97	143	.55	65.7
98	154	.59	77.0

Fig. 10.



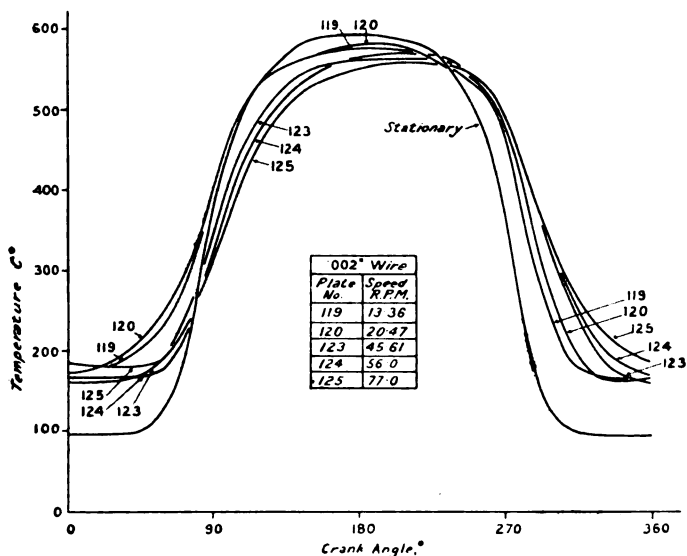
Experimental Curves, .0015 in. measuring wire.

.0015 in. Wire.

Temperature Range 314° C.

Plate. No.	Lag. ° C.	Lag Range	Speed. r.p.m.
104	9.5	.03	25.5
105	19	.06	32.2
107	19	.06	6.9
110	19	.06	58.0
111	19	.06	64.0
112	41	.13	76.5
113	50.5	.16	97.5
114	55	.18	109.0

Fig. 11.



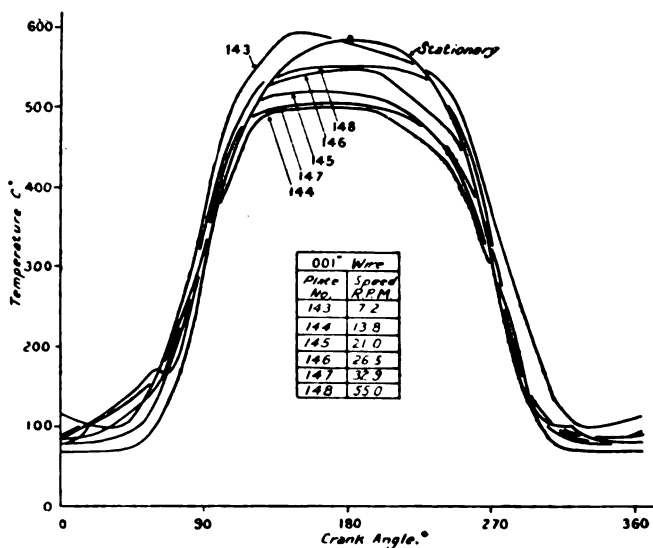
Experimental Curves, .002 in. measuring wire.

.002 in. Wire.

Temperature Range 495°C .

Plate.	Lag.	Lag	Speed.
No.	$^{\circ}\text{C}$.	Range.	r.p.m.
119	15	.03	13.4
120	10	.02	20.5
123	32	.06	45.6
124	28	.06	56
125	40	.08	77

Fig. 12.



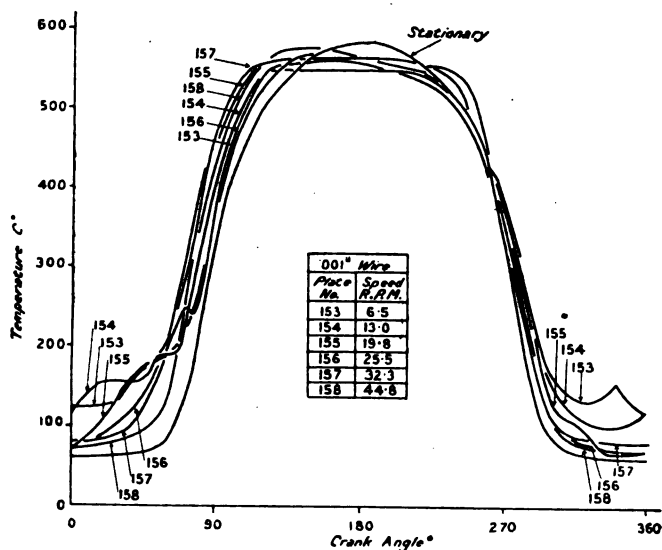
Experimental Curves, .001 in. measuring wire.

.001 in. Wire.

Temperature Range 510° C.

Plate.	Lag.	Lag	Speed.
No.	° C.	Range.	r.p.m.
143	5	.01	7.2
144	88	.17	13.8
145	69	.14	21.0
146	40	.08	26.5
147	81	.16	32.9
148	36	.07	55.0

Fig. 13.



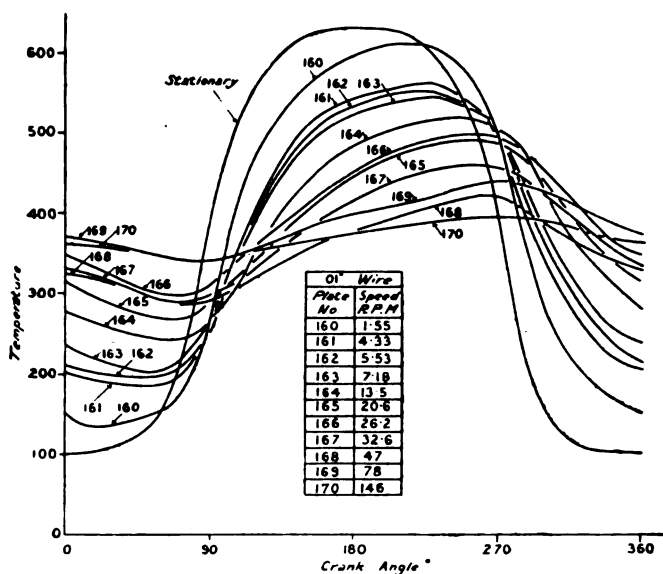
Experimental Curves, .001 in. measuring wire.

.001 in. Wire.

Temperature Range 520° C.

Plate. No.	Lag. ° C.	Lag Range.	Speed. r.p.m.
153	12	.02	6.5
154	36	.07	13.0
155	12	.02	19.8
156	28	.05	25.5
157	22	.04	32.3
158	22	.04	44.8

Fig. 14.



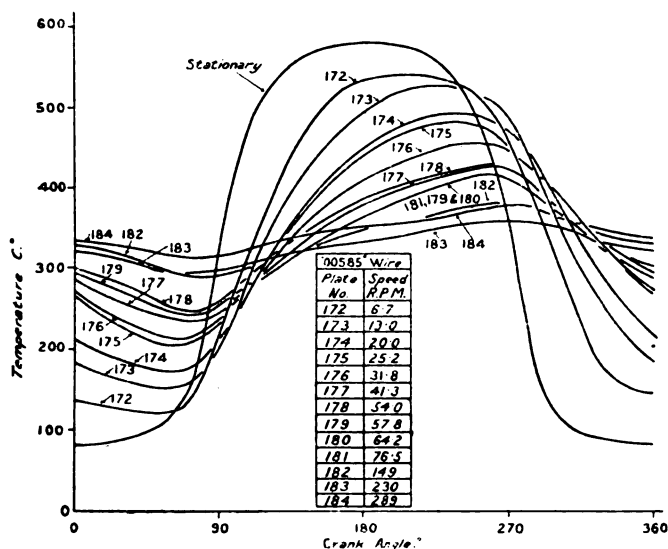
Experimental Curves, .01 in. measuring wire.

.01 in. Wire.

Temperature Range 530° C.

Plate.	Lag.	$\frac{\text{Lag}}{\text{Range}}$	Speed.
No.	° C.		r.p.m.
160	30	.057	1.5
161	87	.164	4.3
162	95	.179	5.5
163	108	.204	7.2
164	145	.274	13.5
165	180	.340	20.6
166	178	.335	26.2
167	210	.396	32.6
168	250	.470	47
169	230	.435	78
170	255	.480	146

Fig. 15.



Experimental Curves, .00585 in. measuring wire.

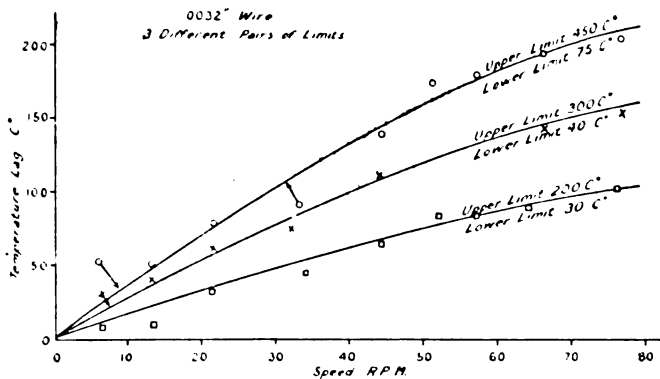
.00585 in. Wire.

Temperature Range 495° C.

Plate No.	Lag. ° C.	Lag Range	Speed. r.p.m.
172	47	.081	6.7
173	83	.143	13.0
174	130	.224	20.0
175	135	.233	25.2
176	170	.293	31.8
177	198	.342	41.3
178	193	.333	54.0
179	211	.364	57.8
180	215	.371	64.2
181	208	.359	76.5
182	230	.397	149
183	245	.423	230
184	229	.393	289

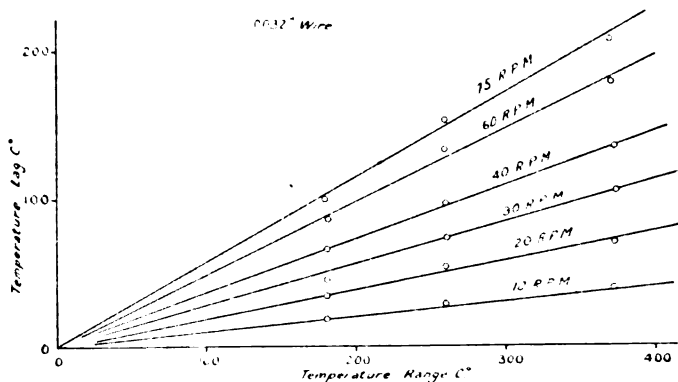
This is plotted in fig. 16 against speed for one diameter of wire ($\cdot 0032$ in.) and three different temperature ranges (370° , 260° , and 180° C.).

Fig. 16.



Curve showing Temperature Lag against Speed for the $\cdot 0032$ in. measuring wire.

Fig. 17.

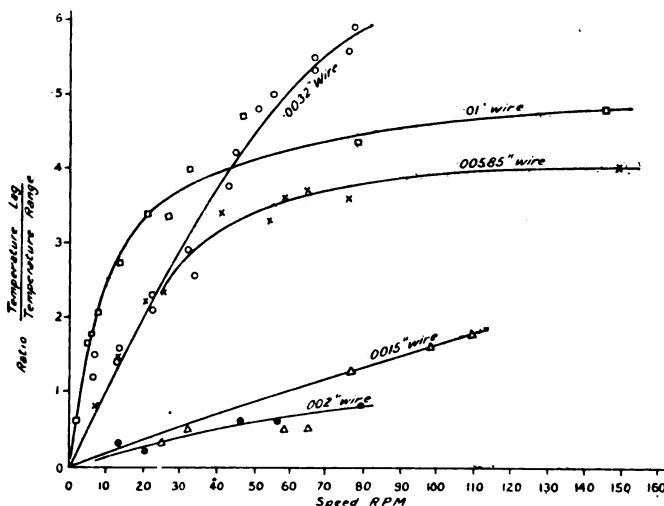


Curve showing Temperature Lag against Temperature Range for the $\cdot 0032$ in. measuring wire.

Fig. 17 shows lag against range for the $\cdot 0032$ in. wire at speeds of 10, 20, 30, 40, 60, and 75 r.p.m. This diagram is constructed from fig. 16. It will be noticed that at all

speeds the ratio of the lag to the range appears to be constant.

Fig. 18.



Curve showing Ratio of Temperature Lag to Temperature Range against Speed for all diameters of measuring wire used.

Assuming this to be true for all diameters of measuring wire, fig. 18 shows the ratio of temperature lag to temperature range against speed for all the diameters of wire used.

It is seen that for low speeds, the temperature lag is nearly proportional to the speed, but at higher speeds it approaches a limit.

The results of the first test on the .001 in. wire were so inconsistent with each other that a second test was carried out, but the results were no better and could not be plotted in fig. 18.

It will be noticed that in successive tests the upper limit of stationary temperature increased, whereas the lower limit remained more or less constant. The shape of the stationary temperature distribution curve also gradually changed, commencing with a flat base and becoming more and more nearly symmetrical. This is taken to be due to the drying of the lagging material which was put round the heating element.

For this reason, the results obtained with the different diameters of wire are not comparable with each other, and it is not possible to draw any conclusions as to how the lag depends on the diameter of the measuring wire.

However, sufficient work has been done to show that, at atmospheric pressure and with comparatively quiescent air, the platinum resistance thermometer is not capable of following with sufficient accuracy temperature changes which take place with the rapidity which obtains in a gas-engine cycle.

It is anticipated that the conditions obtaining in the gas engine cylinder are much more favourable to thermometry on account both of the higher pressures existing and also of the turbulence, and experiments are now being conducted on a gas engine type of apparatus to determine whether this is the case.

CONCLUSION.

The whole of the casting, forging, and machining, besides most of the pattern making required in the construction of the apparatus have been carried out in the Mechanical Engineering Department of the University of Birmingham, and a considerable amount of the authors' time was taken up with this work.

The thanks of the authors are due to the members of the staff of the Workshops of the Department for assistance and facilities given in connexion with the work.

LVII. *Magnetic Rotary Dispersion in Gases.*

By T. H. HAVELOCK, *F.R.S.**

1. **I**N studying the possible influence of anisotropy of the molecule on expressions for the dispersion of magnetic rotation in gases, it appeared that little comparison had been made with observations on the commoner gases such as hydrogen, nitrogen, and oxygen in regions free from absorption. In fact there are not many available results, as experimental work on gases has been chiefly concerned with the relatively large rotations in the neighbourhood of absorption.

In the following notes the point of view is the connexion between ordinary dispersion and that of magnetic rotation, and the comparison with experimental results; the survey covers briefly the various types of formulæ which have been used for the ordinary dispersion of a simple gas. In the first place, a single-term formula for an isotropic static molecule is compared with Siertsema's observations

* Communicated by the Author.

in the visible spectrum. The theory is then extended to an anisotropic static molecule, and the corresponding formulæ deduced; various cases are compared numerically with Sirks' values of the rotation in the ultra-violet. Finally, a similar study is made of the Bohr molecule for hydrogen, following the analysis developed by Sommerfeld and others.

Isotropic Static Molecule.

2. Assume the gas to consist of similar isotropic molecules, each containing a single elastically-bound vibrator of given charge and mass; and suppose further that the refractive index differs little from unity. Then, in the usual notation, the dispersion formula is

$$n^2 - 1 = \frac{4\pi N e^2}{m} \frac{1}{p_0^2 - p^2} = \frac{N e^2}{\pi c^2 m} \frac{1}{\lambda_0^{-2} - \lambda^{-2}}. \quad (1)$$

The corresponding expression for Verdet's constant for the magnetic rotation is

$$V = \frac{2\pi N e^3 p^2}{c^2 m^2} \frac{1}{(p_0^2 - p^2)^2} = \frac{N e^3}{2\pi c^4 m^2 \lambda^2} \frac{1}{(\lambda_0^{-2} - \lambda^{-2})^2}. \quad (2)$$

Further, in this simple case, we have the equivalent expressions :

$$V = \frac{e\lambda}{2c^2 m} \frac{dn}{d\lambda} = \frac{\pi}{2Ne\lambda^2} (n^2 - 1)^2. \quad (3)$$

Extensions of the formulæ have followed the usual course in the theory of dispersion : firstly by having on the left of (1) the quantity $(n^2 - 1)/(n^2 + 2)$ with the corresponding changes in (2) and (3), and secondly by a summation of terms on the right of (1) and (2) to include several natural periods of vibration. The latter extension has chiefly been made in applying a semi-empirical formula like

$$V\lambda^2 = \frac{a_1}{(\lambda_2^{-2} - \lambda^{-2})^2} + \frac{a_2}{(\lambda_2^{-2} - \lambda^{-2})^2} \quad \dots \quad (4)$$

to liquids; in such cases, λ_1 and λ_2 are taken to be the natural wave-lengths of the corresponding dispersion formula, while a_1 and a_2 , which are associated with the Zeeman coefficients for these lines, are left to be determined from experimental values of the magnetic rotation.

For gases when there is no absorption the rotation is
Phil. Mag. S. 6. Vol. 45. No. 267. March 1923. 2 O

small, and this probably accounts for the lack of results obtained under ordinary conditions and extending over any considerable range of wave-length. Apart from the early work of Becquerel and others, there appear to be only two sets of experimental results. We shall consider first those obtained by Siertsema*. The observations were made with the gases under varying high pressures, and were reduced to uniform conditions under the assumption that the rotation is proportional to the density.

3. In Table I. column 2 shows Siertsema's values of Verdet's constant for hydrogen at 9°·5 C. and a pressure of 85 kg./cm.²; the rotations are in minutes and have been multiplied by 10⁶, and the wave-lengths are in $\mu\mu$. Column 3 shows the relative values of $V\lambda^2$, which is the suitable quantity for which to form a dispersion formula; the departure from Biot's law is slight, but regular.

TABLE I.—Hydrogen.

λ .	$V \times 10^6$.	$V\lambda^2$.	From (6).
656	365	1·00	1·00
619	412	1·005	1·004
589	456	1·007	1·008
555	517	1·014	1·014
527	576	1·018	1·019
517	600	1·021	1·021
486	684	1·029	1·029
454	791	1·038	1·038
431	884	1·045	1·047
423	921	1·049	1·050

Siertsema expressed his results by two empirical formulæ, one $a/\lambda + b/\lambda^3$ and the other $a/\lambda^2 + b/\lambda^4$. We use now a formula of the type (2), where λ_0 is derived from a simple dispersion formula. If we take the Cuthbertsons' formula for hydrogen,

$$n^2 - 1 = \frac{3 \cdot 76 \times 10^{-4}}{1 \cdot 378777 - 10^{-10} \lambda^{-2}} \quad \dots \quad (5)$$

we have for the rotation

$$V\lambda^2 = \frac{C}{(1 \cdot 378777 - 10^{-10} \lambda^{-2})^2} \quad \dots \quad (6)$$

The value of λ_0 is 851·6 A.U. Column 4 in Table I. shows the relative values calculated from (6). The agreement is quite satisfactory; hence, as far as this range of

* Siertsema, *Arch. Néerland.* ii. p. 291 (1899)

wave-length is concerned, a single-term formula with the same natural period is sufficient for both dispersions.

In regard to absolute values, there are various possible interpretations. Comparing (1) and (2) with (5) and (6), we may, for instance, regard e and m as the two unknown quantities and thus determine their values for a simple equivalent vibrator which will fit both the ordinary and the rotary dispersion.

Reducing Siertsema's results to absolute measure, we find that at normal temperature and pressure the value of V at the wave-length 656 is 1.335×10^{-9} . Hence, taking $N = 2.70 \times 10^{19}$, we have from (5) and (6) $e^2/m = 3.96 \times 10^8$ and $e^3/m^2 = 1.99 \times 10^{26}$. From these, $e = 7.9 \times 10^{-10}$ and $m = 1.57 \times 10^{-27}$; both values are less than twice the accepted electronic values, but the ratio $e/m = 1.68 \times 10^7$ e.m.u. The usual numerical analysis follows rather different lines. It is more customary to assume, say, the electronic value of e and deduce e/m or the number of valency electrons and so forth, from the various relations between (1) and (2).

4. For nitrogen, Siertsema's values are shown in Table II.; the second column gives V in minutes at 14° C. and 100 kg./cm.², and the third column the relative values of $V\lambda^2$.

TABLE II.—Nitrogen.

λ .	$V \times 10^6$.	$V\lambda^2$.	From (7).
656	439	1.00	1.00
619	495	1.004	1.003
589	548	1.006	1.006
555	620	1.011	1.011
527	691	1.016	1.015
517	719	1.017	1.017
486	818	1.023	1.023
454	946	1.030	1.030
431	1054	1.036	1.037
423	1097	1.039	1.039

The value of λ_0 found by the Cuthbertsons from ordinary dispersion is 725.6 A.U. Using this for the rotation, we obtain values of $V\lambda^2$ which rise too slowly. With unity at 656, the value at 517 is 1.015 and at 423 is 1.036; the differences are no doubt within experimental error, but they are systematic. The fact is that experimental dispersion formulæ for nitrogen do not show very concordant

results when only a single term is used; recent experiments* indicate a considerably higher equivalent value of λ_0 than that found by Cuthbertson. Further, it must be remembered that Siertsema's observations were made at high pressures. In this case, then, we take the relative experimental values of $V\lambda^2$ from Table II., at the wavelengths 656 and 423, and calculate the value of λ_0 ; we obtain thus $\lambda_0 = 759.7$, a rather higher value than the Cuthbertsons' result for ordinary dispersion. With this value, we have

$$V\lambda^2 = \frac{C}{(1.73263 - 10^{-10}\lambda^{-2})^2} \quad \cdot \quad \cdot \quad \cdot \quad (7)$$

The calculated values are shown in column 4 of Table II.

5. We note incidentally the anomalous behaviour of oxygen, which is brought out clearly when we consider $V\lambda^2$ instead of V as is usually the case. Siertsema's values are given in Table III. for oxygen at 7° C. and 100 kg./cm.²

TABLE III.—Oxygen.

λ .	$V \times 10^6$.	$V\lambda^2$.
656	484	1.00
619	523	0.962
589	559	0.931
555	604	0.893
527	646	0.861
517	663	0.851
486	721	0.818
454	799	0.791
431	875	0.781
423	908	0.780

The striking result, shown in the third column, is that $V\lambda^2$ decreases with decreasing wave-length. It is obvious that a single-term formula like (2) is useless in this case. It would be necessary to use an empirical two-term formula like (4), with one of the constants a_1 and a_2 positive and the other negative. It would be possible to represent the course of $V\lambda^2$ in this way, but the range is not sufficient to determine the four constants of such a formula; even if we include later observations by Sirks, which carry the range into the ultra-violet, the results are not sufficiently definite and concordant. In addition, there is no corresponding formula for the ordinary dispersion of oxygen with which to make comparison. The anomalous behaviour of oxygen

* Stoll, *Ann. der Phys.* No. 18 (1922).

may naturally be ascribed to the fact that the gas is paramagnetic; and the suggested occurrence of a term signifying negative rotation may be associated with the reverse action of inter-molecular magnetic fields. In fact, it would be necessary to take into account magnetic properties of the molecule in devising a model to cover such a case.

Anisotropic Static Molecule.

6. In extending the previous formulæ to the ultra-violet, we shall find that the calculated values fall short of the observed dispersion. We proceed to modify the formulæ by taking into account the anisotropy of the molecule—an extension which has already been made in the theory of ordinary dispersion and related phenomena.

The medium is supposed to be a gas, with the refractive index nearly unity, composed of similar molecules for which all orientations are equally probable. Each molecule contains a vibrator of charge e and mass m , whose equilibrium position may be taken as the origin O ; let the principal axes of the molecule for small vibrations be $O(\xi, \eta, \zeta)$, and let $O(x, y, z)$ be fixed directions in space, where the direction-cosines of the two sets of axes are given by the scheme:

	ξ	η	ζ
x	α_1	α_2	α_3
y	β_1	β_2	β_3
z	γ_1	γ_2	γ_3

The external magnetic field H being along Oz , we have

$$(H_\xi, H_\eta, H_\zeta) = (\gamma_1, \gamma_2, \gamma_3)H,$$

and the equations of motion of the vibrator are

$$\left. \begin{aligned} m\ddot{\xi} + mp_1^2\xi &= e\left(E_\xi + \frac{1}{c}\dot{\eta}\gamma_3H - \frac{1}{c}\dot{\xi}\gamma_2H\right), \\ m\ddot{\eta} + mp_2^2\eta &= e\left(E_\eta + \frac{1}{c}\dot{\xi}\gamma_1H - \frac{1}{c}\dot{\xi}\gamma_3H\right), \\ m\ddot{\zeta} + mp_3^2\zeta &= e\left(E_\zeta + \frac{1}{c}\dot{\xi}\gamma_2H - \frac{1}{c}\dot{\eta}\gamma_1H\right) \end{aligned} \right\} \quad . \quad . \quad (8)$$

The two sets of components of electric force are connected by relations of the form

$$E\xi = \alpha_1 E_x + \beta_1 E_y + \gamma_1 E_z, \quad . \quad . \quad . \quad (9)$$

and the components of the displacement by equations like

$$x = \alpha_1 \xi + \alpha_2 \eta + \alpha_3 \zeta. \quad . \quad . \quad . \quad (10)$$

Suppose the electric force to vary as e^{ipt} ; then, writing k for $ipeH/cm$, and a_1 for $p_1^2 - p^2$, etc., the equations (8) give

$$\left. \begin{aligned} a_1 \xi - k\gamma_3 \eta + k\gamma_2 \zeta &= (e/m) E_\xi, \\ k\gamma_3 \xi + a_2 \eta - k\gamma_1 \zeta &= (e/m) E_\eta, \\ -k\gamma_2 \xi + k\gamma_1 \eta + a_3 \zeta &= (e/m) E_\zeta. \end{aligned} \right\} \quad . \quad . \quad . \quad (11)$$

We require to find the mean electric moment of the molecules per unit volume: that is, the mean values of ex , ey , ez in terms of E_x , E_y , E_z for all possible orientations of the axes (ξ , η , ζ). The process consists in solving (11) for ξ , η , ζ , and using (9) and (10). Neglecting powers of k higher than the first, we obtain after reduction

$$\begin{aligned} ex = (e^2/m a_1 a_2 a_3) [& (\alpha_1^2 a_2 a_3 + \alpha_2^2 a_3 a_1 + \alpha_3^2 a_1 a_2) E_x \\ & + \{ \alpha_1 \beta_1 a_2 a_3 + \alpha_2 \beta_2 a_3 a_1 + \alpha_3 \beta_3 a_1 a_2 + k\gamma_1 (\alpha_2 \beta_3 - \alpha_3 \beta_2) a_1 \\ & + k\gamma_2 (\alpha_3 \beta_1 - \alpha_1 \beta_3) a_2 + k\gamma_3 (\alpha_1 \beta_2 - \alpha_2 \beta_1) a_3 \} E_y \\ & + \{ \alpha_1 \gamma_1 a_2 a_3 + \alpha_2 \gamma_2 a_3 a_1 + \alpha_3 \gamma_3 a_1 a_2 + k\gamma_1 (\alpha_2 \gamma_3 - \alpha_3 \gamma_2) a_1 \\ & + k\gamma_2 (\alpha_3 \gamma_1 - \alpha_1 \gamma_3) a_2 + k\gamma_3 (\alpha_1 \gamma_2 - \alpha_2 \gamma_1) a_3 \} E_z], \quad (12) \end{aligned}$$

with similar expressions for ey and ez .

The mean values may be found by expressing the direction-cosines in terms of Eulerian angles θ , ϕ , ψ , and taking the average for all possible values. We have

$$\overline{\alpha_1^2} = \dots\dots\dots - \frac{1}{3}; \quad \overline{\alpha_1 \beta_1} = \dots\dots\dots = 0;$$

$$\overline{\gamma_1 (\alpha_2 \beta_3 - \alpha_3 \beta_2)} = \overline{\gamma_2 (\alpha_3 \beta_1 - \alpha_1 \beta_3)} = \frac{1}{3}; \quad \overline{\gamma_1 (\alpha_2 \gamma_3 - \alpha_3 \gamma_2)} = 0$$

If N is the number of molecules per unit volume, we obtain finally for the components of mean polarization:

$$\left. \begin{aligned} P_x &= \frac{Ne^2}{3m} \frac{1}{a_1 a_2 a_3} \left(E_x \Sigma a_2 a_3 + \frac{ipeH}{cm} E_y \Sigma a_1 \right), \\ P_y &= \frac{Ne^2}{3m} \frac{1}{a_1 a_2 a_3} \left(-\frac{ipeH}{cm} E_x \Sigma a_1 + E_y \Sigma a_2 a_3 \right), \\ P_z &= \frac{Ne^2}{3m} \frac{1}{a_1 a_2 a_3} E_z \Sigma a_2 a_3. \end{aligned} \right\} \quad (13)$$

The refractive index is derived from the relation

$$P/E = (n^2 - 1)/4\pi ;$$

we neglect the influence of neighbouring molecules on the force acting on a vibrator.

In the absence of an external magnetic field, the aggregate behaves like an isotropic medium of refractive index given by

$$n^2 - 1 = \frac{4\pi N e^2}{m} \left(\frac{1}{p_1^2 - p^2} + \frac{1}{p_2^2 - p^2} + \frac{1}{p_3^2 - p^2} \right). \quad (14)$$

With a magnetic field H , parallel to Oz , we have from (13) the usual analysis for waves travelling along Oz ; forming $P_x \pm iP_y$, we obtain the refractive indices for right and left circularly polarized waves:

$$n_{\pm}^2 - 1 = \frac{4\pi N e^2}{m} \left(\sum \frac{1}{a_1} \mp \frac{peH}{cm} \sum \frac{1}{a_2 a_3} \right). \quad (15)$$

Since Verdet's constant is equal to $p(n_- - n_+)/2cH$, we obtain, with the assumption that n is nearly unity,

$$V = \frac{2\pi N e^3 p^2}{3c^2 m^2} \left\{ \frac{1}{(p_2^2 - p^2)(p_3^2 - p^2)} + \frac{1}{(p_3^2 - p^2)(p_1^2 - p^2)} + \frac{1}{(p_1^2 - p^2)(p_2^2 - p^2)} \right\}. \quad (16)$$

These are the direct generalizations of (1) and (2) for an isotropic molecule. It will be noticed that we do not have now formulæ like (3), such as Becquerel's relation; V cannot be expressed directly in terms of n .

If the molecule has an axis of symmetry, so that $p_3 = p_2$, we have

$$n^2 - 1 = \frac{4\pi N e^2}{3m} \left(\frac{1}{p_1^2 - p^2} + \frac{2}{p_2^2 - p^2} \right). \quad (17)$$

$$V = \frac{2\pi N e^3 p^2}{3c^2 m^2} \left\{ \frac{1}{(p_2^2 - p^2)^2} + \frac{2}{(p_1^2 - p^2)(p_2^2 - p^2)} \right\}. \quad (18)$$

We may put these into a form suitable for comparison later with Sommerfeld's formulæ for the Bohr molecule. If

we write $g=1/(p_1^2-p^2)$ and $g'=1/(p_2^2-p^2)$, we have

$$n^2-1 = \frac{4\pi N e^2}{3m} (g+2g'), \quad . \quad . \quad . \quad . \quad . \quad (19)$$

$$V = \frac{2\pi N e^3 p^2}{3c^2 m^2} \left(2gg' + \frac{1}{2p} \frac{dg'}{dp} \right). \quad . \quad . \quad . \quad (20)$$

The influence of asymmetry of the molecule upon magnetic rotation has previously been studied by Gans *, who gives a result of the form

$$V\lambda^2 = \text{const.} \left(\frac{1}{g} + \frac{2}{g'} \right)^{-2} = \frac{\text{const.}}{\left\{ \frac{1}{3} (p_1^2 + 2p_2^2) - p^2 \right\}^2}. \quad (21)$$

This appears to have been obtained by an incorrect method of finding the mean polarization for all possible orientations. Using data for the asymmetry derived from the polarization of scattered light, Gans applies his formulæ to Sierstema's experiments. But we have seen that these are quite well fitted by a simple formula, and we shall see that in this range the difference between formulæ (2) and (18) is quite inappreciable compared with possible experimental error; therefore information about the asymmetry of the molecule cannot be derived from magnetic rotation without observations of greater accuracy or covering a greater range of wave-length.

7. Before discussing numerical results, we may consider briefly the case of a paramagnetic molecule with an intrinsic magnetic moment M . There is now an orientation of the molecule in the magnetic field, so that in averaging the electric moment all orientations are not equally probable. If we assume the magnetic axis to be the axis $O\xi$, the distribution function is

$$e^{MH\gamma_3/kT},$$

where k is the gas constant and T the absolute temperature.

Thus, assuming MH/kT to be small, we must multiply the previous expressions (12) for the electric moment by $1 + MH\gamma_3/kT$ and then take mean values as before. It can easily be verified that the additional terms of the first order in H so obtained do not give any final contribution to the value of the mean polarization. On this theory the orientation of paramagnetic molecules only introduces terms of order

* R. Gans, *Ann. der Phys.* lxxv. p. 119 (1921).

higher than the first. This statement applies to a molecule in which the electric charges vibrate about positions of equilibrium. It is otherwise for a molecule, such as the Bohr model, in which the vibrations are about a steady state of rotation; then orientation affects the magnetic rotation with terms of the first order in H .

8. We turn now to comparison with experiment. Siertsema's work has been extended by Sirks*, whose relative values of V for hydrogen are shown in Table IV.; the corresponding relative values of $V\lambda^2$ are given in the third column.

TABLE IV.—Hydrogen.

λ .	V .	$V\lambda^2$.
578	1.00	1.00
546	1.125	1.003
486	1.44	1.018
436	1.815	1.033
404	2.15	1.054
366	2.64	1.061
313	3.90	1.144
280	5.14	1.210
265	5.975	1.261
253	6.67	1.283
248	7.09	1.305
240	7.76	1.338
238	7.94	1.346

In the first place, $V\lambda^2$ has been calculated for a few wavelengths from the formula (6); these are shown in Table V. The values fall short considerably in the ultra-violet.

I have shown previously† that the ordinary dispersion of hydrogen can be represented by two formulæ of the type (17) over the range 5462 to 1854 A.U.; and that these formulæ also give reasonable agreement with observations on the polarization of scattered light. They are

$$n^2 - 1 = 1.242958 \times 10^{-4} \left\{ \frac{1}{1.032551 - 10^{-10}\lambda^{-2}} + \frac{2}{1.638331 - 10^{-10}\lambda^{-2}} \right\} \quad (22)$$

* J. F. Sirks, *Phys. Zeit.* xiv. p. 336 (1913).

† Proc. Roy. Soc. A, ci. p. 154 (1922).

and

$$n^2 - 1 = 1.2429583 \times 10^{-4} \left\{ \frac{1}{2.088392 - 10^{-10}\lambda^{-2}} + \frac{2}{1.169513 - 10^{-10}\lambda^{-2}} \right\}. \quad (23)$$

From (18) the corresponding formulæ for $V\lambda^2$ are

$$V\lambda^2 = \frac{C}{(1.6383 - x)} \left\{ \frac{1}{1.6383 - x} + \frac{2}{1.0325 - x} \right\}, \quad (24)$$

and

$$V\lambda^2 = \frac{C}{(1.1695 - x)} \left\{ \frac{1}{1.1695 - x} + \frac{2}{2.0884 - x} \right\}, \quad (25)$$

where x has been put for $10^{-10}\lambda^{-2}$.

The calculated values are shown in the third and fourth columns of Table V.

TABLE V.—Calculated $V\lambda^2$.

λ .	(6)	(24)	(25)	(27)
578	1.00	1.00	1.00	1.00
436	1.034	1.035	1.037	1.030
280	1.161	1.167	1.171	1.139
248	1.230	1.239	1.245	1.201
238	1.259	1.270	1.275	1.227

The values are better than those from (6), but they still fall much short of Sirks' values in the smaller wave-lengths. There are various reasons for not accepting the comparison as conclusive, but taking it as it stands it would seem that the model of (22) and (23) does not include fully the dispersion of magnetic rotation. Comparing (22) and (23) with (17), we find that if e and m have their electronic values, and if there are two electrons per molecule, then the constant 1.243 in (22) and (23) should have been 1.606; the smaller value denotes coupling between the two electrons. There is perhaps no reason to expect that the magnetic rotation should be expressed accurately by the same equivalent vibrator as for ordinary dispersion or other electrical effects. This suggests trying a dispersion formula

for hydrogen in which the constant has the accepted electronic value. One of this character has been given by Lundblad*; it was obtained by regarding the molecule as made up of two interacting doublets. When put into partial fractions and expressed in wave-lengths, it becomes

$$\frac{n^2 - 1}{n^2 + 2} = \frac{1.605896 \times 10^{-4}}{3} \left\{ \frac{1}{0.976725 - 10^{-10} \lambda^{-2}} + \frac{2}{2.977210 - 10^{-10} \lambda^{-2}} \right\}. \quad (26)$$

This formula fits the ordinary dispersion well in the range 546 to 230, but, as I have shown previously, it does not agree with observations on the polarization of scattered light. Treating it as of type (17), the corresponding magnetic rotation should be

$$V\lambda^2 = \frac{C}{(2.9772 - x)} \left\{ \frac{1}{2.9772 - x} + \frac{2}{0.9767 - x} \right\}. \quad (27)$$

Calculated values are shown in the last column of Table V.; the agreement with observation is much worse than for (22) and (23).

But it is quite possible that the experimental results are not suitable for elaborate analysis. It should be remarked that the dispersion formulæ (22) and (23) were derived from the dispersion of hydrogen under usual conditions, while for the magnetic rotation the gas was under a pressure of 70–90 atmospheres; further, different samples of gas gave rather different results. It may be that the ordinary dispersion was different under these conditions; in fact, Sirks, in attempting to deduce e/m from his results by a formula like (1) or (2), assumes the natural wave-length λ_0 to be 870, which is appreciably higher than the value 851 of Cuthbertson's formula (5) or than the mean in either (22) or (23). Further, this difference is in the right direction for accounting for the discrepancy. This opinion is confirmed if we use the Becquerel formula (3) and calculate $V\lambda^2$ as proportional to $\lambda^3 dn/d\lambda$. Seeing that (22) and (23) represent the dispersion of hydrogen with great accuracy, this is equivalent to calculating $V\lambda^2$ from a formula of the

* Lundblad, *Untersuch. über die Optik*, p. 192 (1920).

type (4), in which the natural vibrations specified by λ_1 and λ_2 are treated as due to independent vibrators with the same Zeeman coefficient. The calculation gives the ratio 1.3 for the extreme wave-lengths instead of the observed value 1.346, and it seems that any modification like (24) or (25) should give a less value than 1.3. Before attempting any further analysis, it would be desirable to have parallel sets of observations of ordinary and rotary dispersion carried out, if possible, on the same gas under similar conditions.

Bohr Hydrogen Molecule.

9. To complete this survey it is of interest to make the same comparison for the Bohr molecule, as an example of vibrations about steady motion, in contrast to the previous static molecules. It is not our intention to criticize the defects of the original Bohr model, or the foundations of the dispersion theory: for the latter, one may refer to a recent critical study by Epstein*. The theory of dispersion and of magnetic rotation has been developed by Sommerfeld† and by Pauer‡, from whose work we quote the results necessary to illustrate the points in question, making some slight changes in notation.

Using the notation of § 6, with Oζ as the line joining the two nuclei of the molecule, the components of electric moment of the molecule in the absence of any external magnetic field are given by

$$\left. \begin{aligned} P_{\xi} &= -\frac{e^2}{m\rho_0^2} \left[\frac{1}{2} \{f(x) + f(-x)\} E_{\xi} + i \frac{1}{2} \{f(x) - f(-x)\} E_{\eta} \right], \\ P_{\eta} &= -\frac{e^2}{m\rho_0^2} \left[\frac{1}{2} \{f(x) + f(-x)\} E_{\eta} - i \frac{1}{2} \{f(x) - f(-x)\} E_{\xi} \right], \\ P_{\zeta} &= -\frac{2e^2}{m\rho_0^2} \phi(x) E_{\zeta}, \end{aligned} \right\} \quad \dots (28)$$

where $x = \rho/\rho_0$.

Here ρ_0 is the angular velocity of the two ring-electrons in the steady state, and is determined by applying the

* P. S. Epstein, *Zeit. für Phys.* ix, p. 92 (1922).

† A. Sommerfeld, *Ann. der Phys.* liii, p. 497 (1917).

‡ F. Pauer, *Ann. der Phys.* lvi, p. 261 (1918).

quantum rule to each electron ; the numerical value so found is 4.55×10^{16} .

The small vibrations about the steady state are assumed to follow the ordinary laws of dynamics, and the functions f and ϕ in (28) are found in this way from the equations of motion of the ring-electrons for forced vibrations of frequency p . It may be noted that the molecule, so defined, is dynamically unstable. For hydrogen,

$$\left. \begin{aligned} f(x) &= \frac{(x-2)^2 + 0.15479}{(x-1)^4 - 1.69042(x-1)^2 - 0.607197}, \\ \phi(x) &= \frac{1}{x^2 - 0.30958}. \end{aligned} \right\} \quad (29)$$

With all orientations of the molecule equally probable, the refractive index follows from (28) by the usual method of averaging, with the result

$$n^2 - 1 = -\frac{8\pi N e^2}{3m p_0^2} \{f(x) + f(-x) + \phi(x)\}, \quad (30)$$

where e and m are the charge and mass of a single electron.

When there is an external magnetic field, the application of the quantum rule is a point that requires further investigation. For various reasons, Sommerfeld and Pauer in their analysis use the rule as determining the steady state only in the absence of a magnetic field. The small vibrations are determined from the equations of motion. Apart from the form of the functions f and ϕ , the analysis proceeds on similar lines to that for a static molecule ; the resulting expression for Verdet's constant for hydrogen is

$$V = \frac{4\pi N e^3}{3c^2 m^2} \frac{p}{p_0^3} [x\phi(x)\{f(x) + f(-x)\} - \frac{1}{4}\{f'(x) - f'(-x)\}]. \quad (31)$$

The functions ϕ and f are associated with axial vibrations and those in the plane of the ring respectively ; if we put

$$g = -\phi(x)/p_0^2; \quad g' = -\{f(x) + f(-x)\}/2p_0^2, \quad (32)$$

then g and g' correspond to the same quantities as in § 6.

Equation (30) is now

$$n^2 - 1 = \frac{8\pi N e^2}{3m} (g + 2g'), \quad . \quad . \quad . \quad (33)$$

and (31) reduces to

$$V = \frac{4\pi N e^2 p^2}{3c^2 m^2} \left(2gg' + \frac{1}{2p} \frac{dg'}{dp} \right). \quad . \quad . \quad . \quad (34)$$

These results are of the same form as (19) and (20) for the static molecule, as might have been expected, since the quantum rule was only used to define the steady state.

10. There is, however, a notable difference between the two cases if the medium is paramagnetic. Here again, as in § 7, we have to multiply the expressions for the electric polarization by $1 + MH\gamma_3/kT$, before taking mean values. But there remain now terms of the first order; Sommerfeld's expression for Verdet's constant is (31) with an additional term within the square brackets, namely

$$(mcM/2kT)\{f(x) - f(-x)\}. \quad . \quad . \quad . \quad (35)$$

Numerical calculation shows that for oxygen this new term is many times greater than the other terms of (31); in fact, the same remark would hold for the Bohr hydrogen molecule. Sommerfeld avoids the difficulty by concluding that paramagnetism is atomic and not molecular, so that orientation does not affect directly the orbits which are under consideration in the theory of dispersion.

It is obvious that the difference from the static molecule arises from the fact that the medium would have intrinsic rotational properties if the molecules were not orientated at random. If, for instance, we imagine the axes of the molecules to be all in the same direction, without considering any other effects that might be produced, it follows from (28) that the medium would be rotational with a gyric coefficient

$$\frac{2\pi N e^2 p}{mc p_0^2} \left\{ f\left(\frac{p}{p_0}\right) - f\left(-\frac{p}{p_0}\right) \right\}. \quad . \quad . \quad . \quad (36)$$

A numerical estimate for the hydrogen molecule shows that this would have an enormous value compared with actual rotational coefficients.

11. For comparison with experimental results, Sommerfeld expanded (30) and (31) in powers of x and used the first

two terms of the expansion in each case ; it was found that the values agreed fairly well with the ordinary dispersion, and also with Siertsema's results for magnetic rotation, provided p_0 was taken as 4.51×10^{16} instead of the supposed quantum value 4.55×10^{16} .

The calculations are now extended to the ultra-violet, using the exact formula (31) with $p_0 = 4.51 \times 10^{16}$ and f and ϕ as in (29). The relative values of $V\lambda^2$ are shown in the second column of Table VI., and may be compared with Sirks' results given in Table IV.

For absolute values we take the wave-length 656. We saw in § 3 that Siertsema's value for V is 1.335×10^{-9} ; the formula (31) gives 1.2×10^{-9} .

The comparison between the formula (30) and ordinary dispersion has been extended recently to the ultra-violet by Gans *, using the experimental values of Kirn. Gans finds that the dispersion, apart from absolute values, is fitted more accurately by taking $p_0 = 4.3 \times 10^{16}$. Calculating now the magnetic rotation from (31) with this value of p_0 , we find the relative values of $V\lambda^2$ as given in the third column of Table VI.

TABLE VI.—Values of $V\lambda^2$.

λ .	$p = 4.51$.	$p_0 = 4.3$.
578	1.00	1.00
436	1.033	1.036
280	1.183	1.206
238	1.297	1.336

The new value of p_0 gives a better agreement with Sirks' results for the relative rotary dispersion ; but this has been obtained by some sacrifice as regards absolute values both for the ordinary and the rotary dispersion. With the accepted values of N , e , and m , and with $p_0 = 4.3 \times 10^{16}$, the values of $n^2 - 1$ from (30) are about 10 per cent. greater than Kirn's experimental values ; further, the corresponding value of Verdet's constant at wave-length 656 is 1.454×10^{-9} , which is larger than Siertsema's value. Another way of expressing the divergence is by calculating $dn/d\lambda$ from (30) or (33) ; the ratio of $\lambda^3 dn/d\lambda$ at the wave-lengths 238 and

* R. Gans, *Zeit. für Phys.* ix. p. 81 (1922).

578 is found to be 1.378, which is considerably higher than the value 1.3 obtained in § 8 from Kirn's results. In any case it appears that, in order to make (30) and (31) agree with observed results, it is necessary to treat them as formulæ with two or three disposable constants; the theory then loses its value as one giving results directly in terms of known electronic constants.

Summary.

12. A comparison is made between the ordinary dispersion of certain gases and the dispersion of magnetic rotation in regions free from absorption. It is shown that formulæ derived from a simple static molecule with one type of vibrator are sufficient for both dispersions in the visible spectrum for gases like hydrogen and nitrogen. On the other hand, the case of oxygen, in which $V\lambda^2$ decreases with decreasing wave-length, indicates the necessity of including the magnetic properties of the molecule before a complete theory can be formed.

Omitting paramagnetic effects, expressions for the rotary dispersion are obtained for an anisotropic static molecule, such as has been used for the ordinary dispersion of hydrogen. Two formulæ of this kind are compared with Sirks' observations in the ultra-violet; the modification improves the agreement, but not to a sufficient extent.

Similar conclusions are reached after a numerical study of the Bohr molecule for hydrogen, following Sommerfeld's analysis of the ordinary and magnetic dispersion.

It is pointed out that in all cases the adjustable constants of the ordinary dispersion formulæ were found by comparison with experiments on gases under ordinary conditions of temperature and pressure; while the available data for magnetic rotation were obtained from gases under high pressures. It may well be the case that the results are not strictly comparable; and it is desirable that parallel sets of observations should be made on the same gas under similar conditions.

LVIII. *The Sum of Series of Cosecants.* By G. N. WATSON, Sc.D., F.R.S., Professor of Mathematics in the University of Birmingham*.

1. **I**N a paper on Atomic Systems recently published in this Magazine by Mr. R. Hargreaves †, the series

$$S_n^{(1)} \equiv \sum_{m=1}^{n-1} \operatorname{cosec} \frac{m\pi}{n}, \quad S_n^{(3)} \equiv \sum_{m=1}^{n-1} \operatorname{cosec}^3 \frac{m\pi}{n},$$

where n is a large integer, were encountered in the course of the analysis. I have already published ‡ an investigation of the asymptotic expansion of the former, with a table of numerical values, and, in view of the interest aroused in the latter by Mr. Hargreaves's researches, I propose to investigate it by the same methods. I must admit that my methods are of a slightly more recondite nature than the elementary methods used by Mr. Hargreaves; but, to compensate for this, they give complete asymptotic expansions, and, moreover, they indicate the nature of the asymptotic expansion when any odd powers of the cosecants, other than the first and third, are involved.

The result contained in my former paper was

$$\pi S_n^{(1)} \sim 2n \log_e (2n) + 2n(\gamma - \log_e \pi) + 2 \sum_{m=1}^{\infty} \frac{(-)^m B_m}{m \cdot (2m)!} \frac{\pi^{2m} (2^{2m-1} - 1)}{n^{2m-1}}.$$

In this formula, γ is Euler's constant, $B_1, B_2, B_3, \dots$ are the numbers of Bernoulli, while the error due to stopping at any term of the series is of the same sign as, and numerically less than, the first term neglected.

2. To investigate $S_n^{(3)}$ we twice differentiate Euler's formula

$$\int_0^{\infty} \frac{x^{a-1} dx}{1+x} = \frac{\pi}{\sin a\pi}, \quad (0 < a < 1)$$

with respect to a , and get

$$\int_0^{\infty} \frac{(\log x)^2 x^{a-1} dx}{1+x} = \frac{\pi^3}{\sin^3 a\pi} (2 - \sin^2 a\pi).$$

* Communicated by the Author.

† Phil. Mag. (6) vol. xliv. pp. 1065-1105 (1922).

‡ Phil. Mag. (6) vol. xxxi. pp. 111-118 (1916).

Phil. Mag. S. 6. Vol. 45. No. 267. March 1923. 2 P

It follows at once that

$$\begin{aligned}
 2\pi^3 S_n^{(3)} - \pi^3 S_n^{(1)} &= \int_0^\infty \frac{(\log x)^2}{x(1+x)} \{x^{1/n} + x^{2/n} + \dots + x^{(n-1)/n}\} dx \\
 &= \int_0^\infty \frac{(\log x)^2 (x^{1/n} - x)}{x(1+x)(1-x^{1/n})} dx \\
 &= n^3 \int_0^\infty \frac{(\log y)^2 (1-y^{n-1})}{(1+y^n)(1-y)} dy \\
 &= n^3 \int_{-\infty}^\infty \frac{t^2 (1-e^{-(n-1)t})}{(1+e^{-nt})(e^t-1)} dt \\
 &= 2n^3 \int_0^\infty \frac{t^2 (1-e^{-(n-1)t})}{(1+e^{-nt})(e^t-1)} dt,
 \end{aligned}$$

when we sum the geometrical progression and then write $x^{1/n} = y = e^{-t}$; the final step, of bisecting the range of integration, is justified by the consideration that the integrand is an even function of t .

3. To obtain the asymptotic expansion of the last integral we proceed much as in my former paper, the analysis being simplified by the presence of the factor t^2 in the numerator.

We re-write the integrand thus:

$$\frac{t^2(1-e^{-(n-1)t})}{(1+e^{-nt})(e^t-1)} = \frac{t^2}{e^t-1} - \frac{2e^{-nt}}{1+e^{-nt}} \left\{ \frac{t^2}{e^t-1} + \frac{t^2}{2} \right\},$$

and if, for brevity, we put

$$\frac{1}{1^n} + \frac{1}{2^n} + \frac{1}{3^n} + \dots = \sigma_n,$$

we have

$$\begin{aligned}
 \int_0^\infty \frac{t^2 dt}{e^t-1} &= \sum_{r=1}^\infty \int_0^\infty t^2 e^{-rt} dt \\
 &= 2! \sum_{r=1}^\infty r^{-3} \\
 &= 2\sigma_3.
 \end{aligned}$$

Again we have

$$\begin{aligned}
 \frac{t^2}{e^t-1} + \frac{t^2}{2} &= t + B_1 \frac{t^3}{2!} - B_2 \frac{t^5}{4!} + \dots + (-)^{r-1} B_r \frac{t^{2r+1}}{(2r)!} \\
 &\quad + (-)^r \theta B_{r+1} \frac{t^{2r+3}}{(2r+2)!},
 \end{aligned}$$

where $0 \leq \theta \leq 1$; and so we get

$$\begin{aligned} 2\pi^3 S_n^{(3)} - \pi^3 S_n^{(1)} &= 4\sigma_3 n^3 - 4n^3 \int_0^\infty \frac{t dt}{e^{nt} + 1} \\ &\quad + 4n^3 \int_0^\infty \frac{dt}{e^{nt} + 1} \left\{ \sum_{m=1}^r (-)^m B_m \frac{t^{2m+1}}{(2m)!} \right. \\ &\quad \left. + (-)^{r+1} \theta B_{r+1} \frac{t^{2r+3}}{(2r+2)!} \right\}. \end{aligned}$$

When we make use of the formula

$$\int_0^\infty \frac{u^m du}{e^u + 1} = m! (1 - 2^{-m}) \sigma_{m+1},$$

which was established in my former paper, we find, on writing u in place of nt ,

$$\begin{aligned} 2\pi^3 S_n^{(3)} - \pi^3 S_n^{(1)} &\sim 4\sigma_3 n^3 - 2n\sigma_2 \\ &\quad + 4 \sum_{m=1}^{\infty} \frac{(-)^m (2m+1) B_m (1 - 2^{-2m-1}) \sigma_{2m+2}}{n^{2m-1}}, \end{aligned}$$

the error due to stopping at any term being of the same sign as, and numerically less than, the first term neglected.

Replacing σ_{2m+2} by $2^{2m+1} \pi^{2m+2} B_{m+1} / (2m+2)!$, and substituting for $S_n^{(1)}$ the expansion quoted in § 1, we find that

$$\begin{aligned} \pi^3 S_n^{(3)} &\sim 2\sigma_3 n^3 + \pi^2 n \log_e n + \pi^2 n (\gamma - \tfrac{1}{6} - \log_e \tfrac{1}{2} \pi) \\ &\quad + \sum_{m=1}^{\infty} \frac{(-)^m B_m \pi^{2m+2}}{(2m)! n^{2m-1}} \left\{ \frac{2^{2m-1} - 1}{m} B_m + \frac{2^{2m+1} - 1}{m+1} B_{m+1} \right\}, \end{aligned}$$

the series possessing the usual property concerning the magnitude and sign of the remainder.

For purposes of tabulation this expansion may be written in the form

$$\begin{aligned} S_n^{(3)} &= n^3 \times 0.07753 \ 63592 \ 05833 \ 59787 \\ &\quad + (n \log_{10} 2n) \times 0.73293 \ 55992 - n \times 0.23369 \ 70348 \\ &\quad - n^{-1} \times 0.07417 \ 64932 + n^{-3} \times 0.01561 \ 93435 \\ &\quad - n^{-5} \times 0.01319 \ 98 + n^{-7} \times 0.04576. \end{aligned}$$

From these numerical results, the following table was constructed, with the exception of the entries for $n=2, 3, 4, 5$,

which were calculated directly and not from the asymptotic expansion :—

n .	$S_n^{(3)}$.	n .	$S_n^{(3)}$.
2	1.00000	25	1236.79111
3	3.07920	26	1389.40079
4	6.65685	27	1554.11838
5	12.17352	28	1731.40865
6	20.07920	29	1921.73639
7	30.82881	30	2125.56643
8	44.88014	35	3363.52172
9	62.69282	40	5008.77095
10	84.72770	45	7119.43774
11	111.44650	50	9753.65213
12	143.31156	55	12969.54859
13	180.78572	60	16825.26489
14	224.33215	65	21378.94118
15	274.41434	70	26688.71951
16	331.49599	75	32812.74338
17	396.04101	80	39809.15746
18	468.51343	85	47736.10739
19	549.37746	90	56651.73956
20	639.09736	95	66614.20104
21	738.13754	100	77681.63944
22	846.96244	360	3618206.17062
23	966.03660	1000	77538544.95112
24	1095.82461		

4. If the formula

$$\int_0^\infty \frac{x^{a-1} dx}{1+x} = \frac{\pi}{\sin a\pi}$$

is differentiated $2r$ times with respect to a (r being any assigned positive integer) it is easy to prove by the methods already used that the dominant term of the asymptotic expansion of

$$\sum_{m=0}^{n-1} \operatorname{cosec}^{2r+1} \frac{m\pi}{n}$$

is $2\pi^{-2r-1} \sigma_{2r+1} n^{2r+1}$ ($r \geq 1$).

In like manner it may be found from the formula

$$P \int_0^\infty \frac{x^{a-1} dx}{1-x} = \frac{\pi}{\tan a\pi}$$

that the dominant term of the series for

$$\sum_{m=0}^{n-1} \operatorname{cosec}^{2r} \frac{m\pi}{n}$$

is $2\pi^{-2r} \sigma_{2r} n^{2r}$, which is equal to

$$(2n)^{2r} B_r / (2r)!$$

But, since the values of $\operatorname{cosec}^2(m\pi/n)$, for acute values of $m\pi/n$, are the roots of the equations

$$x^{\frac{1}{2}n-1} - \frac{n^2-2^2}{3!} x^{\frac{1}{2}n-2} + \frac{(n^2-2^2)(n^2-4^2)}{5!} x^{\frac{1}{2}n-3} - \dots = 0,$$

$$x^{\frac{1}{2}(n-1)} - \frac{n^2-1^2}{3!} x^{\frac{1}{2}(n-3)} + \frac{(n^2-1^2)(n^2-3^2)}{5!} x^{\frac{1}{2}(n-5)} - \dots = 0,$$

(according as n is even or odd), it is evident that the series for

$$\sum_{m=0}^{n-1} \operatorname{cosec}^{2r} \frac{m\pi}{n}$$

terminates, and that it is a polynomial in n^2 of degree r in which the coefficients can be calculated with sufficient labour for any assigned value of r .

LIX. *A simple Form of Apparatus for observing the Rate of Reaction between Gases and Liquids, and its Use in determining the Rate of Solution of Oxygen by Water under Different Conditions of mixing.* By H. G. BECKER, A.R.C.Sc.I., A.I.C., Demonstrator in Chemistry, Royal College of Science, Dublin *.

I. INTRODUCTION.

THE apparatus described in this paper was primarily devised as an alternative method of carrying out the "Five Days' Dissolved Oxygen Absorption Test," and is based on a principle previously utilized by Prof. Adeney for the same purpose †.

In the course of the work, however, it became apparent that the principle was capable of wider application, and the apparatus was finally designed with a view to its possible use for the study of gas-liquid systems in general.

The effect of different rates of stirring on the rate of solution of oxygen in water has been determined by means of the apparatus, and the results of the experiments are given in this communication, as they have a direct bearing on some previously published work ‡.

* Communicated by Prof. W. E. Adeney, A.R.C.Sc.I., D.Sc. Reprinted from the Proceedings of the Royal Dublin Society, vol. xvi. (n.s.).

† Fifth Report, Royal Commission on Sewage Disposal, Appendix vi. p. 438.

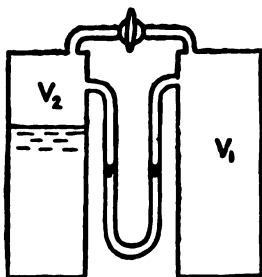
‡ Adeney and Becker, Scientific Proc. R. D. S. xv. p. 609 (1919).

II. THE PRINCIPLE ON WHICH THE APPARATUS IS BASED.

The principle utilized in the apparatus depends on the changes in pressure which occur when a liquid is placed in contact with a closed volume of a gas which it is capable of absorbing, and the action of the apparatus will be understood by reference to fig. 1.

In the system shown in the diagram there is a volume of gas V_2 , connected through a manometer with a volume of gas V_1 , there being sufficient liquid in V_1 to ensure saturation of the gas with vapour, and the liquid under test is in contact with the gas in V_2 . When the tap is closed, any absorption of gas by the liquid from V_2 , results in a decrease in pressure, which is indicated on the manometer, and from

Fig. 1.



the manometer reading the volume of gas absorbed can be calculated. With such an arrangement it is possible to vary the sensitivity of the manometer considerably. The smaller the volume V_2 becomes in comparison with V_1 , the greater the movement of the manometer (within limits) for a given absorption of gas by the liquid. Further, when the tap connecting V_2 and V_1 is opened the manometer returns to zero, and the difference in pressure previously existing in V_2 is distributed between the combined volume, thus making it a much smaller fraction of the whole. With such an arrangement it becomes possible to reset the manometer to zero several times during the course of an experiment, without allowing the pressure in V_2 to fall to such a value as would seriously affect the solubility of the gas. The tap also affords an easy method of replenishing the supply of one of the constituent gases of a mixture contained in V_2 . Thus, if V_2 contains atmospheric air in contact with a liquid absorbing oxygen, and V_1 contains pure oxygen, then, after a given absorption, the opening of tap resets the manometer,

and also replaces the oxygen absorbed to an extent which will depend on the ratio $\frac{V_2}{V_1}$.

The conditions at the start of an experiment are such that the pressures in V_1 and V_2 are equal to each other and to the atmospheric pressure P mm.

Now, suppose an absorption of Q c.c. takes place in V_2 , and that the resulting manometer reading is p mm., then $(V_2 - Q)$ c.c. at P are occupying $(V_2 - v_1)$ at P_z , where v_1 = the volume of liquid which has risen above the zero point in the manometer, and V_1 c.c. at P are occupying $(V_1 + v_1)$ c.c. at P_y .

Now, since $P_y = P_z + p$,

$$\therefore \frac{PV_1}{V_1 + v_1} = \frac{P(V_2 - Q)}{V_2 - v_1} + p,$$

which gives

$$Q = v_1 \frac{(V_2 + V_1)}{V_1 + v_1} + \frac{p}{P} (V_2 - v_1).$$

If the two vessels are now connected by opening the tap, P_y becomes equal to P_z , and $p = 0$.

There is then $V_1 + (V_2 - Q)$ c.c. at P occupying a volume $V_1 + V_2$ at P_z .

Hence

$$\begin{aligned} P_z &= \frac{P(V_1 + V_2 - Q)}{V_1 + V_2} \\ &= P \left(1 - \frac{Q}{V_1 + V_2} \right). \end{aligned}$$

Hence the pressure in the air spaces after resetting the manometer will be less than that existing at the start by a quantity dependent on the ratio of the volume of gas absorbed to the combined volume of the two air spaces. By making the latter large this quantity can be made very small at will.

III. DESCRIPTION OF APPARATUS.

The apparatus which was devised on this principle is shown diagrammatically in fig. 2.

It consists of two cylindrical glass vessels about 30 mm. in diameter, which are connected to two branches of a three-way tap. The lower vessel is of such a size as to contain a suitable volume (say, 100 c.c.) of liquid to be tested, and still leave room for an air space of about 50 c.c.; the upper vessel also has a capacity of about 50 c.c. The three-way

tap allows of the two air spaces being connected through the manometer, or directly, according to its position. Hence, when an absorption has taken place, the manometer can be reset to zero by suitably turning the tap.

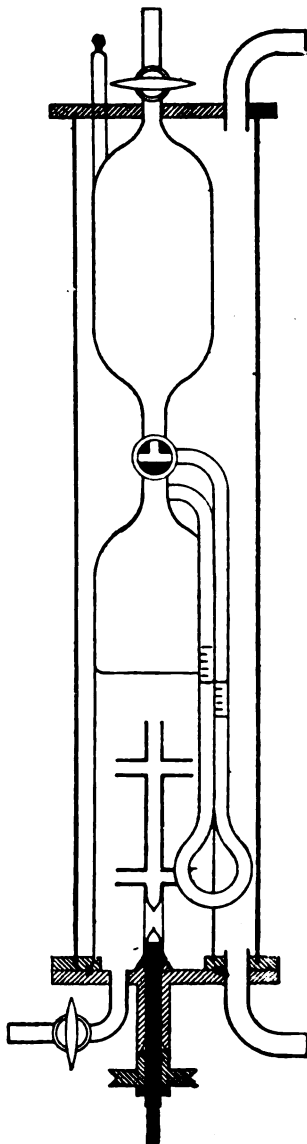
The whole apparatus, including the manometer, is enclosed in a cylindrical water-jacket, through which water is circulated from a thermostat. The handle of the three-way tap projects through a hole blown in this water jacket, the joint being kept water-tight by means of a rubber diaphragm. The water-jacket is closed at each end by flanges, which may be made of brass, tin, or ebonite, according to the purpose for which the apparatus is to be used.

The stirrer passes through a long sleeve in the lower flange, and is provided with two conical surfaces, one of which can be adjusted by means of a screw, so that the whole is water-tight. In addition, the glass part of the stirrer is expanded into a cone at the lower end, which is ground to fit a corresponding cone on the bearing, so that the metallic parts of the stirrer do not come into contact with the liquid at any point.

The glass part of the stirrer is so designed that, when rotated at a high speed, it causes a stream of fine bubbles of the gas to circulate through the liquid, thus ensuring equilibrium between the liquid and the gas.

The manometer is provided with a scale of millimetres etched on the glass.

Fig. 2.



IV. CALIBRATION OF THE APPARATUS.

In order to check the formula derived for the calculation of the volume of gas absorbed, use was made of ferrous hydrate as an absorbent for oxygen. The following experiments were made :—

The apparatus was filled with 110 c.c. of distilled water which had been previously saturated with air at 20° C. by bubbling air through it for some hours, and the water circulation from the thermostat through the water-jacket started. When everything was in equilibrium, about 25 c.c. of the water was withdrawn, and in place of it was added exactly 10 c.c. of a solution of ferrous sulphate containing 8.2 grams per litre, followed by 10 c.c. of a 10 per cent. solution of sodium carbonate, the whole being carefully washed into the apparatus. The barometer was then read, and the taps of the apparatus having been suitably adjusted, the stirrer was started, and the manometer watched until the reading became constant. The maximum reading was then used to calculate the volume of oxygen absorbed by the ferrous hydrate.

Experiment A.—Temperature, 20.0° C ; barometer, 768.1 mm.

Maximum reading of manometer 114.0 divisions.

Second reading after resetting to zero. 5 5 „

114 divisions at 768.1 mm. correspond to 1.525 cm.

5.5 „ „ „ „ .073 „

Total ... 1.598

Total volume absorbed, calculated for N.T.P. = 1.504 c.c.

Experiment B.—Temperature, 20° C.; barometer, 769.9 mm.

Maximum reading of manometer, 118 divisions.

118 divisions at 769.9 mm. correspond to 1.610 c.c., which at N.T.P. reduces to 1.520 c.c.

The mean of the two experiments gives 1.512 c.c. absorbed.

Since the partial pressure of the oxygen in the air in the vessel was reduced from $\frac{10.5}{50}$ to $\frac{9.0}{50}$, a correction for this must be applied. The pressure in the vessel before the experiments was 768.1 mm., and at the end was 758.0 mm.

Taking the composition of atmospheric air to be approximately : nitrogen, 79 per cent., oxygen, 21 per cent., and the coefficient of absorption of oxygen as 0.0310 at 20° C., we can calculate the amounts of oxygen in solution at the beginning and at the end of the experiments.

The pressure of aqueous vapour at 20.0° C. is 17.5 mm.

The volume of oxygen in solution at the start is :

$$V_0 = .0310 \times 110 \times \frac{10.5}{50} \times \frac{750.6}{760} = .706 \text{ c.c.}$$

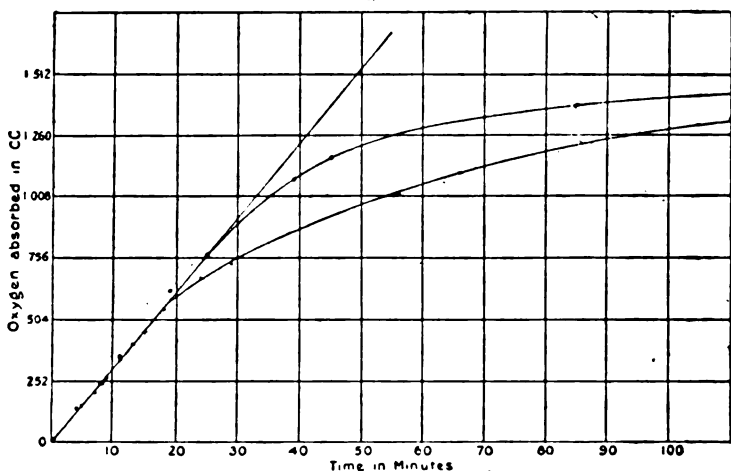
The volume in solution at the end is :

$$V_1 = .0310 \times 110 \times \frac{9}{50} \times \frac{740.5}{760} = .598 \text{ c.c.}$$

Hence the difference due to change in the saturation value is .108 c.c., and this, when added to the volume indicated by the manometer reading, gives a total of 1.62 c.c. as the actual absorption.

The 10 c.c. of ferrous sulphate used should have absorbed 1.64 c.c. oxygen according to its titre by potassium permanganate, hence the two values agree within $\frac{1}{4}$ per cent.

Fig. 3.



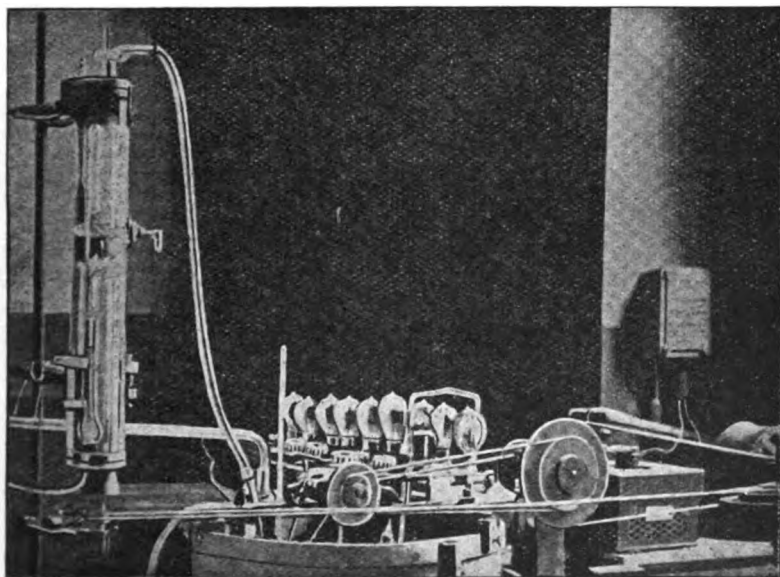
The graph, fig. 3, shows the course of the absorption. During the first part of the absorption the water is completely de-aerated by the excess of ferrous hydrate, and, consequently, the oxygen is absorbed at a constant rate, as shown by the fact that the graph at this portion is practically a straight line. In the second stage, when all the ferrous hydrate has been oxidized, the absorption falls off gradually, so that the graph becomes a logarithmic curve. During this stage the water becomes completely re-aerated. In the figure, the second graph shows a more gradual approach to saturation than the first; this is due to the fact that during this

experiment the speed of the motor driving the stirrer varied suddenly owing to variation in the voltage of the supply. This observation indicated the advisability of determining the time necessary to attain equilibrium under certain conditions. As this was intimately connected with some work which had been done previously on the rate of solution of gases by water, it was considered worth while to examine it more fully.

V. EXPERIMENTS ON THE EFFECT OF STIRRING ON THE
RATE OF SOLUTION OF OXYGEN IN WATER.

The method consisted in introducing into the apparatus known amounts of a solution of ferrous sulphate and precipitating the hydrate by means of a solution of caustic

Fig. 4.



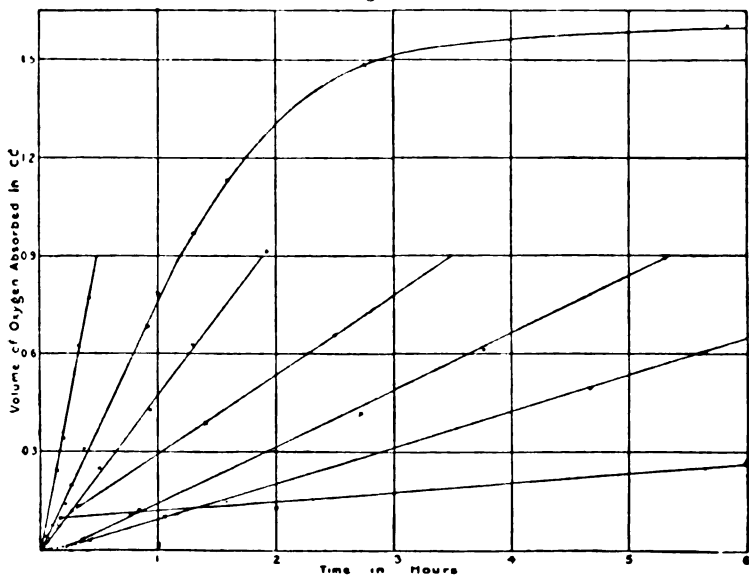
potash ; the stirrer was then driven at certain definite speeds by means of a small alternating-current motor (which could be relied upon not to vary in speed to any large extent), and the rate at which the oxygen was absorbed noted by observing the manometer.

The complete apparatus used for these experiments is shown in the photograph (fig. 4). The motor at the right of the picture drives the small circulating pump (which is

immersed in the water in the thermostat), and also a stirrer in the thermostat. The water is pumped along the horizontal glass tube to the left, and into the water-jacket of the apparatus already described, from which it returns to the thermostat by the rubber tube from the top.

To the extreme right will be seen one of a series of horizontal pulleys which we connected to the small alternating-current motor in order to give the desired variation in speed of stirring. This pulley is connected to the stirrer of the apparatus by the long belt appearing in the foreground, thus imparting motion to the stirrer at a rate which could be determined by the ratio of the various pulleys. The water

Fig. 5.

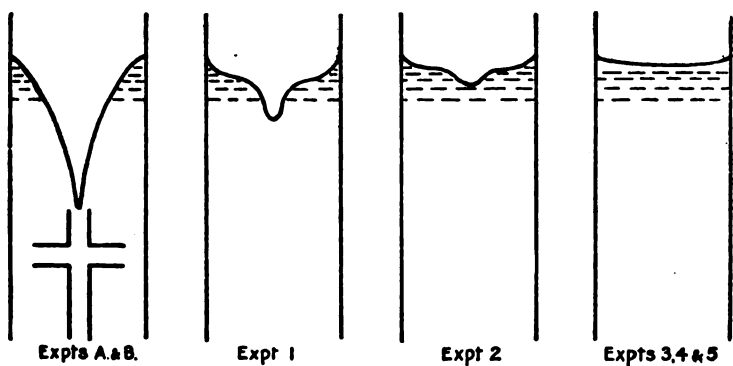


circulation was continued, and the stirrer run at a constant speed during the course of each experiment. The lower speeds of revolution were counted directly, using a stop-watch to check the time, and for the higher speeds the rate of one of the slower-moving pulleys was found and that of the stirrer by calculation.

Five experiments were made with different rates of stirring, and one experiment was made to compare the rate at which quiescent water absorbs oxygen with the rates at which the thoroughly stirred water absorbs it. The results of these experiments are shown in fig. 5.

The rate of stirring in these experiments varied from zero to about 1000 revolutions per minute. The lower rates up to about 140 revolutions per minute did not appreciably distort the surface of the water, but above this speed the surface varied in shape and area with each variation in the speed of the stirrer. The shapes assumed by the water surface are shown in fig. 6; and it will be seen that they range from the nearly flat surface of still water to the point at which the air is drawn down into the water in small bubbles. At this point the surface area becomes uncertain, so that no conclusions can be drawn from experiments at higher speeds. In the other cases the surface area was taken to be approximately equal to that of a cone with the

Fig. 6.



vertical axis equal in depth to that attained by the lowest point of the water surface.

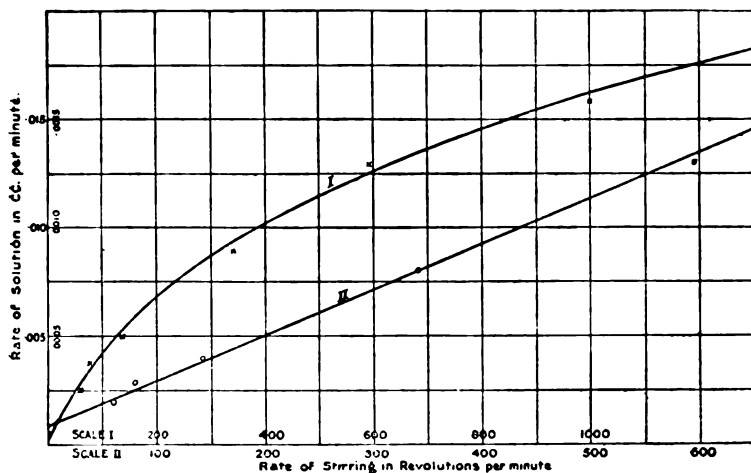
The progress of the absorption followed a linear law, as will be seen from the graph, fig. 5, and this shows that the ferrous hydrate de-oxygenated the water completely almost at once, so that the rate of solution of the oxygen remained constant until all the hydrate was oxidized.

The variation in the value of the rate of solution with stirring is shown in the table and in fig. 7. On the graph the lower line shows the rate of solution under the conditions of the experiment plotted against rate of stirring, and the points lie approximately on a straight line. Hence under the conditions of these experiments the rate of solution varies directly as the rate of stirring.

Values of Rate of Solution for different Rates of Stirring.

Experiment.	Speed of stirrer, r.p.m.	Estimated areas of surface, sq. cm.	Rate of solution in c.c. per min.	Rate of solution per unit area. $S = \frac{a}{A}$.
A and B.	1000	19.0	.030	.0016
1	590	11.1	.014	.0013
2	340	8.8	.008	.0009
3	140	8.1	.004	.0005
4	80	8.1	.003	.0004
5	60	8.1	.002	.00025
6	0	8.1	.0001	.00001

Fig. 7.

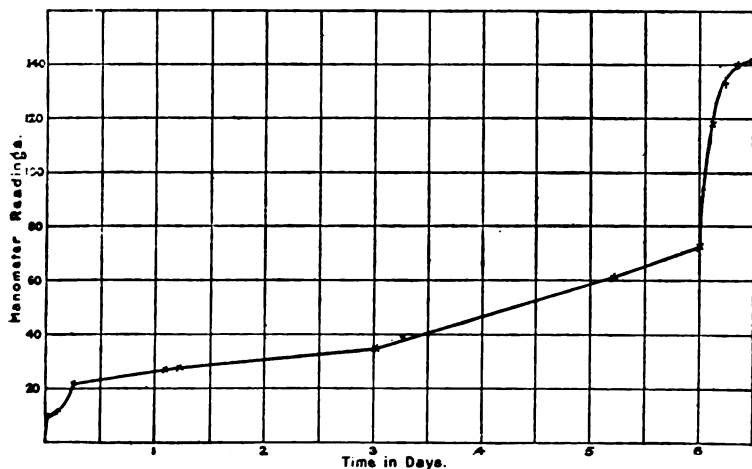


When, however, the effect of increased surface area is taken into account, and the rate of solution per unit area plotted against rate of stirring, the result is the upper line in fig. 7. This curve shows the rapid increase in the rate of solution at first, which gradually falls off as the higher values are reached, and tends to reach a maximum.

VI. COMPARISON OF RESULTS.

The results obtained in Experiment 6 are shown as a graph in fig. 8 in order to afford a comparison between the rate at which the oxygen is absorbed by quiescent water and the rate when the water is stirred. The water was at first stirred for two minutes in order to mix the ferrous hydrate with the liquid, and thus reduce the oxygen content to zero. During this period the rate of absorption was of the same order as obtained in the other experiments. The stirring was then stopped, and the rate fell off slowly as the liquid

Fig. 8.



came to rest until it reached a value which remained nearly constant for three days. On the third day this suddenly changed to a higher value, which remained constant until the sixth day, by which time only about half the saturation value had been reached. The liquid was then stirred again, and the remainder of the absorption was completed in about five hours. Hence a process of absorption which may take many days to complete when the water is quiescent takes place in as many hours with moderate stirring.

The sudden change in the rate of solution of oxygen by the quiescent water indicated above is characteristic of the process under these conditions, for the rate of solution of gases by water is then liable to sudden and unaccountable variations within narrow limits.

The greatest value for the rate of solution per unit area

given in the table represents the maximum rate attainable under the conditions of these experiments, without allowing the surface exposed to become indefinite: hence it is of interest to compare this with the rate of solution as determined in previous experiments*.

The rate of solution of oxygen into air-free water has been found by a totally different method to be $\cdot 0161$ c.c. per minute per square centimetre of area exposed. Hence for the oxygen in the atmosphere the rate should be $\cdot 0161 \times \frac{21}{100} = \cdot 0034$ c.c. per minute under similar conditions, since the rate of solution has been shown to be proportional to the partial pressure.

This value is more than twice as great as the maximum value attained in these experiments ($\cdot 0016$), showing that the rate of mixing that was reached under these circumstances was not so rapid as that obtaining in the experiments referred to. This was to be expected, since in those experiments the water was exposed to the oxygen in very thin layers, and very perfectly mixed immediately afterwards. However, the fact that the two values come so near each other shows that with more perfect stirring arrangements it might be possible to approximate very closely to the maximum rate of solution.

These experiments therefore afford a connecting-link between the conditions obtaining in the work referred to and those obtaining in nature. They also emphasize the important part played by mixing of the water in determining the rate of solution. It will be seen on reference to the table that very gentle stirring of the under layers of the water increases the rate of solution as much as twenty-fold as compared with the stationary water. This bears out the view put forward previously †, that the rate of solution of air by water under ordinary conditions is largely determined by the rate of mixing. Experiments are being continued with this apparatus; and it is hoped to publish further results in the future.

Chemical Department,
Royal College of Science, Dublin.

* Adeney and Becker, Scientific Proc. R. D. S. xv. p. 625 (1919).

† Adeney and Becker, Scientific Proc. R. D. S. xvi. p. 143 (1920).

LX. *Some Photoelectric Experiments on Platinum relating to the Influence of Gases.* By LARS A. WELO, Ph.D.*

AMONG the problems in connexion with the photoelectric effect it seems that none has led, for so long a time, to such conflicting experimental results and hence to so wide a difference of opinion as that concerning the influence of gases. Among those who dissent from the prevailing view that gases are merely of secondary influence are to be mentioned, particularly, Hallwachs and his students†. The reason for the differing results and opinions is, I believe, that attention has been directed too much towards the entire elimination of gases without a study of the change in photo-sensitiveness when the gas is being removed. The complete removal of gas is extremely difficult and is always a questionable achievement. A more certain procedure would seem to be to observe the changes of photo-sensitiveness accompanying a gradual removal of gas and then, by a sort of process of passing to the limit, on the basis of the observed changes, draw conclusions as to the effect to be expected when all the gas is removed.

This plan has been adopted by M. Sende and H. Simon‡ at the suggestion of Hallwachs. By heating a platinum foil in a vacuum at fixed high temperatures, they have obtained the sensitiveness as a function of the time of heating. Discontinuing the experiment at too early a stage and consequently approaching the limit on the basis of incomplete data, they have come to conclusions that must be said to be quite erroneous.

Another procedure on this principle is that first used by Piersol§ and later by myself||. The metal foil is heated at various increasing heating currents and the photo-sensitiveness is determined after the foil has become cool. The curve showing the sensitiveness as a function of the heating current with which gas was driven off, exhibits marked maxima and minima. The experiments herein described are of this type and may be regarded as in continuation of those previously reported upon, under improved experimental conditions.

* Communicated by Professor Gustaf Granqvist.

† See, among other papers: G. Wiedemann and W. Hallwachs, *Verh. d. D. Phys. Ges.* xvi. p. 107 (1914); W. Hallwachs, *Phys. Zeit.* xxi. p. 561 (1920); H. Küstner, *Phys. Zeit.* xv. p. 68 (1914); M. Sende and H. Simon, *Ann. d. Phys.* lxx. p. 697 (1921).

‡ *Ann. d. Phys.* lxx. p. 697 (1921).

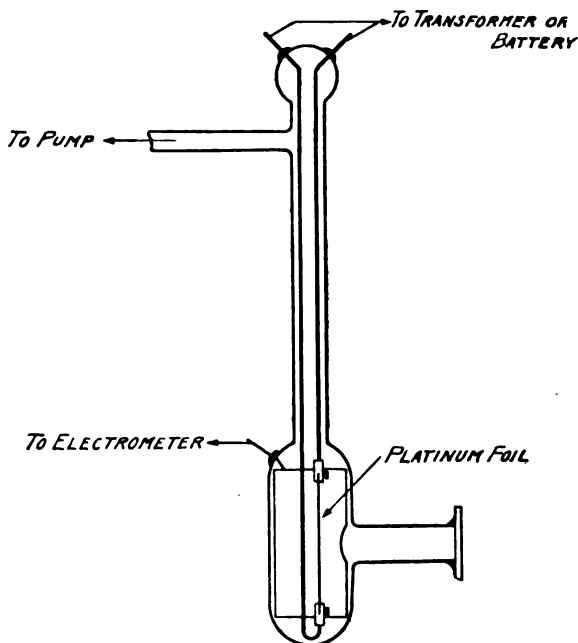
§ *Phys. Rev.* viii. p. 238 (1916).

|| *Phys. Rev.* xii. p. 251 (1918).

The original aim was two-fold. First, to work in much higher vacua in order to eliminate possible effects of residual gases. Second, to use two extreme wave-lengths for which platinum is sensitive, rather than the total radiation; making possible, not only conclusions as to the manner in which gas affects the photoelectric effect, but also as to the structure of the adsorbed layer. As the work proceeded, it became apparent that time is quite as important a factor in the removal of occluded and adsorbed gases as high temperatures and high vacua. Accordingly, heating-current-photo-current curves were obtained after the platinum had been heated in a vacuum for a very long time. On the basis of the changed type of curve thus obtained, the principal conclusion is drawn: namely, that the platinum itself is the seat of electronic emission and that the layer of gas at the surface merely hinders their escape.

The Apparatus and Method of Experiment.

Fig. 1.



In the early part of the work when emphasis was placed on very high vacua and the fullest possible elimination of vapours, the tube shown in fig. 1 was used. All glass joints

were blown, as was also the direct connexion to the Volmer condensation pump. A hard white sealing-wax was used to attach the quartz plate. Eight sealed-in platinum leads entered the tube at the top and were welded in groups of four to the iron wires supporting the platinum foil. The receiving electrode was an oxidized copper cylinder completely surrounding the foil, except for a small opening to admit the radiation. The platinum foil was 6 cm. long, 3.4 mm. wide, and 0.08 mm. thick.

Fig. 2.

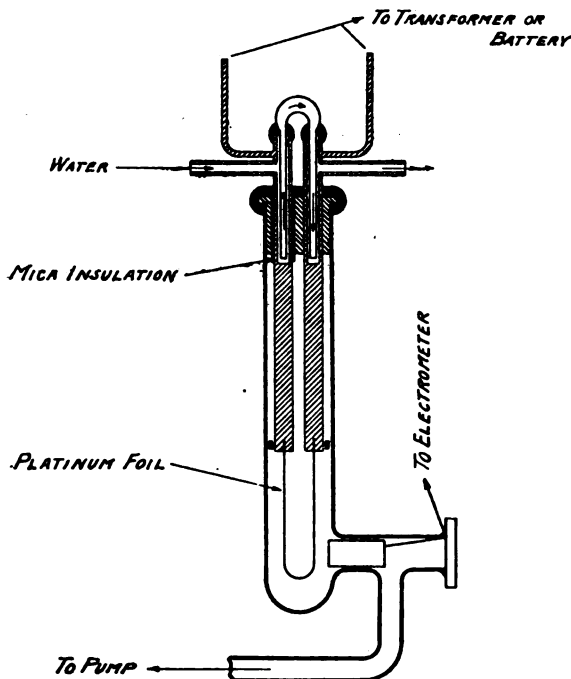


Fig 2. shows the tube used later, when it was known that residual gases and vapours at low pressures play a negligible part, and when some cooling arrangement was necessary while heating for a long time. It was designed to make use of longer foils in order to reduce the effects of gas diffusion from the cold ends. The foils were of the same width and thickness as before, but 13 cm. long and mounted in the form of a U. The receiving electrode was a copper cylinder slipped into the side tube admitting the radiation. The brass rods passed through a brass stopper closely fitting the

glass tube. One of the rods was insulated with mica. Picein was used to make the joints tight and also to attach the quartz plate.

The Volmer condensation pump was backed by a Gaele mercury and oil pump. A McLeod gauge between the pumps showed that the back pressure on the condensation pump was easily kept less than 6×10^{-5} mm. of mercury when the foil was not being heated. From observations with the induction-coil discharge it is known that the pressures in the tubes were much smaller. During a run the condensation pump was continually operated. The other pumps were only run from time to time to keep the back pressure small. When the foil was to be heated, connexion was made to a step-down transformer. When the photoelectric current was to be measured, the transformer connexion was broken and connexion made with the negative pole of a 125 volt battery so that saturation was certain. The currents were measured by the high resistance method. The resistance of about 4.5×10^9 ohms was a fine, long capillary tube containing a 10 per cent. solution of alcohol in xylol. The electrometer had a sensibility of 520 mm. per volt at 1.5 metres distance. A Heraeus quartz mercury lamp served as source of radiation. Its constant power consumption was frequently checked during a run. The slit-width of 1.5 mm. was rather large, so that the light, after passing through the Hilger monochromator, was not strictly monochromatic. In view of the decided differences obtained with the extreme wave-lengths employed it was not deemed necessary to have the light purely monochromatic. Ten minutes was adopted as the standard time of heating with each current, although times of 5 or 7 minutes gave the same type of curve. The photoelectric currents were generally measured two minutes after heating was stopped. In the latter stages of the work when the foils were more nearly gas-free, the photo-sensitiveness was rather unsteady, and it was necessary to wait until a fairly constant value was reached.

Independence of Degree of Evacuation.

As remarked in the foregoing, a heating-current-photo-current curve shows marked maxima and minima. The process of getting rid of gas seems to be accompanied by some complicating features. One would expect that the photo-sensitiveness should gradually increase or that it should remain constant beyond a certain heating-current.

In my former paper* I discussed a possible explanation if one supposes that active layers are built up from residual gases and vapours whose effect is superposed upon that of the metal; or, that a destructive layer from the same source is the cause of the depressions in the curve. The curves of fig. 3† afford a test on this point when compared with the previously published curves of Piersol and myself. The vacua of the present experiments were of the order 10^{-6} mm. of mercury and at least 100 times better than before. The variations beyond the first maximum should thus be much less marked if not entirely absent. In fact, they are still enormous and fully as pronounced as in the former work. The source of the disturbing gas-layer is, then, the occluded or dissolved gas in the platinum itself, and not that which remains in the tube. This result was confirmed later in that the irregularities in the curves disappeared after heating and pumping for several hours.

In fig. 3 the curves to the left are for the original run on a piece of platinum subjected to no treatment, aside from washing in acid and distilled water, followed by thorough drying. The curves to the right are for the same foil after it had stood, for 40 hours, in dry air admitted immediately after completing the original run. It will be shown in a following section of this paper that air has little or nothing to do with the shapes of these curves. Except in their first part, similar curves would have been secured if the second run had been made immediately on completing the first. It will be noted that the first maximum in the left-hand curve is not fully developed. The peak was missed since no observation was made at 2 amperes of heating-current.

Differences with respect to Wave-lengths.

The possibilities in the way of explaining the varying sensitiveness observed in a heating-current-photo-current curve may be summarized as follows:—

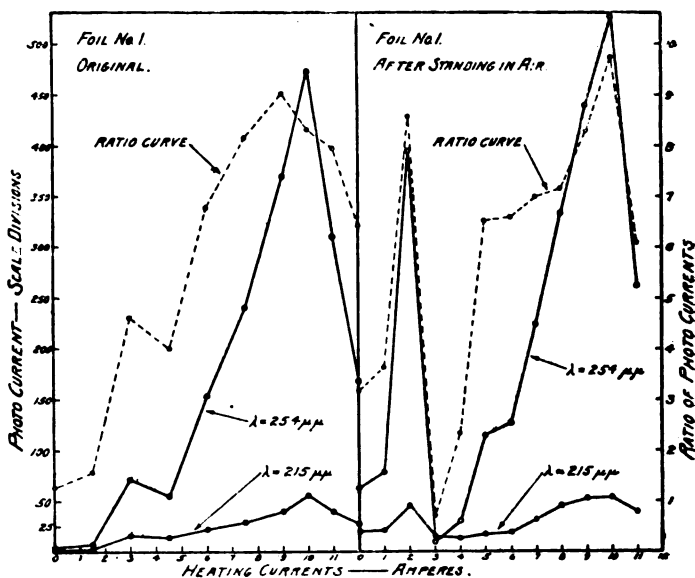
- (1) Change of Photoelectric property of Metal.
 - (a) Chemical combination with gas.
 - (b) Change of gas concentration.
- (2) Absorption of a Constant Initial Emission.
 - (a) Transition Layer theory of Adsorption.
 - (b) Layer one molecule thick.

* *Loc. cit.*

† The smaller heating-currents shown here are due to the use of narrower foils.

The first possibility is readily tested by observations on the long wave limit at various heating-currents. No shift of the wave-length limit was observed, either during the runs shown in fig. 3, or in any of the later runs made on other foils. Special effort was made to detect such changes at the peaks of the curves or at heating-currents corresponding to low sensitiveness. Similar results with respect to constant wave-length limits have been reported by Koppius*, although the absolute value of the photo-current from pure platinum

Fig. 3.



varied somewhat with the temperature and very much with time. Possibility (1) is thus excluded and with it the need of deciding between (a) and (b). This statement is, of course, subject to the validity of the general rule that the photoelectric wave-length limit is a characteristic constant for an element or a compound.

If, during an experiment of this sort, we make observations with two extreme wave-lengths instead of the total radiation, it is possible to decide between the cases (a) and (b) of the remaining possibility. In the transition layer theory of

* Phys. Rev. xviii. p. 443 (1921).

adsorption the gas is assumed to constitute a miniature atmosphere at the surface. Cleaning of the substance is looked upon as a decrease in the thickness or density of the adsorbed layer. In the primary valence theory the layer is imagined to be, on the whole, only one molecule thick, and cleaning must be thought of as the opening up of gaps or clean patches on the surface.

The differences with respect to the effect on the electron emission is apparent. In the case of the transition layer there will be selective absorption with regard to the electron's velocity. The relative proportion of slow and fast electrons breaking through the layer and reaching the receiving electrode will depend on the stage of cleaning. On the other hand, if cleaned patches are formed on the surface, all of the emitted electrons, fast or slow, reach the receiving electrode, while all of the electrons emitted from the gas-covered metal are stopped. If one is to assume a layer of molecular thickness at all one must also make this last assumption in order to account for the low sensitiveness before cleaning, even with short wave-length radiation.

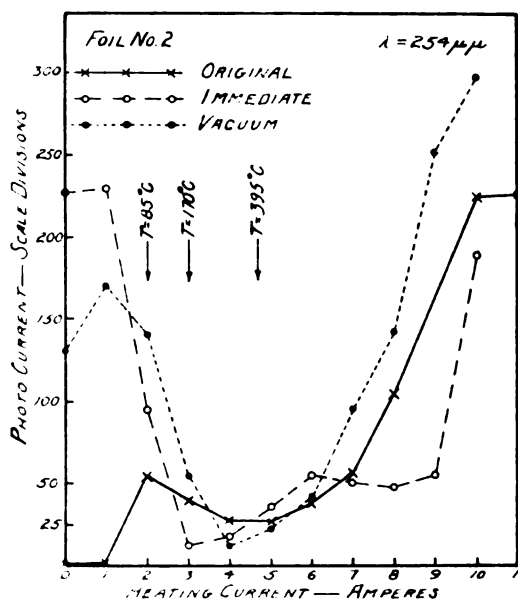
The ratio of the photo-current for the long-wave radiation to the photo-current for radiation of short wave-length thus becomes the test between the two theories of adsorption. The relative intensities of the two radiations must, of course, be constant. Since the slower electrons are absorbed, the peaks and the depressions in the curves should be more prominent in those for radiation of long wave-length. The ratio, at each heating-current, of the two photo-currents will not be constant but will be larger when the sensitiveness is high. If, on heating, clean patches are formed, the photo-emission for each wave-length is proportional to the total clean area and the ratio should be the same at all heating-currents.

The results of this test are shown in fig. 3. The conditions under which the data were taken are described in the preceding sections. The observations with the two radiations were, of course, made during the same runs and for each heating-current, at as nearly the same time as possible. The scale of ratios is at the right. They are seen to vary from less than one to almost 10, so that the test is decisively against the primary valence theory of adsorption. There must be an atmosphere of more than molecular thickness, or some equivalent system, which sifts out the slowly moving electrons.

Repeated runs on the same Foil.

Fig. 4 shows the original and two typical repetition curves for a new foil. "Immediate" means that the run was made immediately after completing the previous run. "Vacuum" means that the foil had stood in the exhausted tube for some time following the previous run or heating, in this case 91 hours. The lower absolute values of the photo-currents, as compared with fig. 3, are due partly to the use of another foil and partly to the fact that another tube (see fig. 2) was employed. In this tube the receiving

Fig. 4.



electrode is placed in front of the foil and does not completely surround it so that some of the electrons may miss the electrode. The original and immediate curves are consecutive, while the vacuum curve is for the fifth run. Similar immediate and vacuum curves were obtained even after a dozen runs had been made, showing that the disturbing gas is not removed during one or even several runs. In each succeeding run, however, the minimum at 4 amperes of heating-current becomes less and less marked. Time is required as well as high vacua and temperatures in order to remove the gases.

The Temperatures.

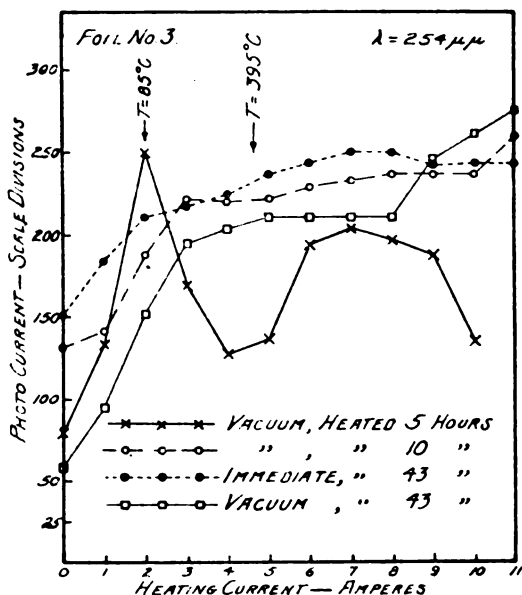
In fig. 4 and the succeeding figures the approximate temperatures corresponding to the most interesting parts of the curves are given. They are taken from a calibration curve determined by fusing small bits of substances of known melting-points on the foils when the work was completed. The heating-current necessary to raise the foil to the melting temperature was noted. The substances were: paraffine, $42^{\circ}5$ C. ; sulphur, $112^{\circ}5$ C. and potassium bichromate, 395° C. The heating-currents at melting were, respectively, 1.13, 2.42, and 4.63 amperes. The temperature corresponding to a heating-current of 11 amperes is estimated to be about 1300° C. The maximum heating current was as high as possible consistent with a barely perceptible evaporation of the platinum.

Continued Heating at High Temperatures.

In fig. 5 we see the importance of time as a factor in the removal of occluded or dissolved gases. Foil No. 3 was cut from the same sheet and adjoining foil No. 2. Since the same tube (fig. 2) was employed, the absolute values of the photo-currents are comparable with those shown in fig. 4. The heating was done at 11 amperes. It was not continuous, and the times indicated merely show the total time of heating. A vacuum curve taken after 5 hours of heating shows the usual minimum, but it is not so well developed. When the total time of heating is extended to 10 hours the minimum in a curve has disappeared. Now, for the first time, a curve of the expected form is realized: namely, one showing an increase in photo-sensitiveness at first and an approach to constancy at the larger heating-currents. It was expected that by heating for a still longer time, the vacuum and especially the immediate curve should show greater constancy of photo-sensitiveness during a run. The vacuum curve after heating 43 hours is not essentially different from that secured after 10 hours of heating. Contrary to expectation, the immediate curve shows that the foil is not at its highest sensitiveness immediately after a long period of heating. The gradual rise is not accidental, for it was observed during other similar runs. In the vacuum curves the gradual rise is due to the removal of the fatigue effect introduced by the residual air which is present in the tube in very small amounts. In a following section it will be seen that so large a fatigue does not occur in the presence of other gases.

The curves of fig. 5 represent, it is believed, the closest possible approach to the "ideal" heating-current-photo-current curve. It is not claimed that the gases are entirely absent, but the remaining quantities are so small after 10 or more hours of heating that not enough remains to develop the minima so prominent in the original and in the repetition curves. Further, the fundamental photoelectric current for platinum is seen to be that of the maxima in the earlier

Fig. 5.



curves. There is seen to be, always, in these curves of fig. 5, an approach to the limiting sensitiveness of about 250 scale divisions under the existing experimental conditions. The limiting value is never zero.

The Gases Emitted.

The gases driven from the foil were frequently examined with a spectroscope during the 43 hour-period of heating. The condensation pump forced them into a large bulb in connexion with a Geissler discharge-tube of small volume. With mercury, the gases in the bulb were compressed into the discharge-tube to suitable pressures. During the first 12 hours of heating the only lines or bands to be seen were those of carbon dioxide. According to Kayser* the same spectrum is given by carbon monoxide. After 12 hours of

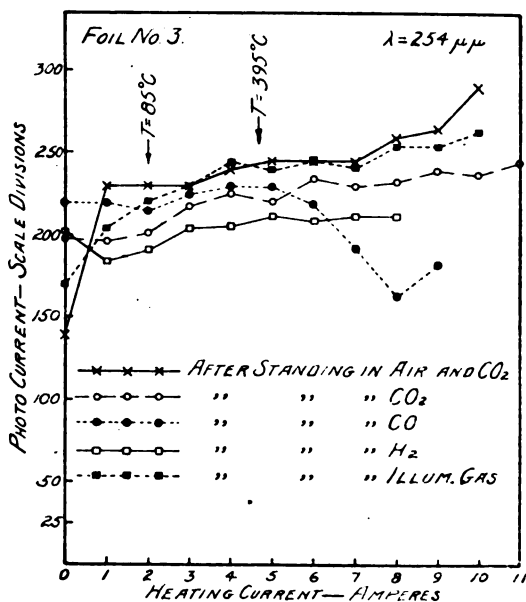
* *Handbuch der Spektroskopie.*

heating the carbon compounds disappeared and the hydrogen lines alone were seen. A marked diminution of the rate of gas emission also occurred when their character changed.

Gas Treatment not Effective.

The attempt was made to reintroduce the irregularities in the curves by letting the gas-free foil stand in gas from 1 to 4 days. In view of the spectroscopic results it was natural to try the oxides of carbon and hydrogen and finally air. As these gases failed to introduce the irregularities, particularly the minimum at 4 amperes of heating-current, an

Fig. 6.



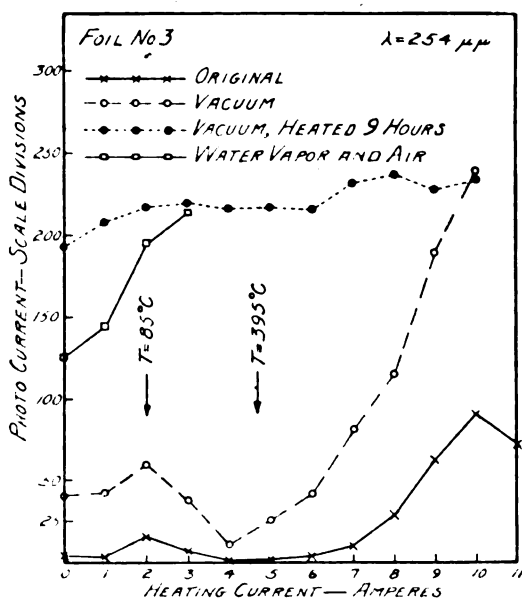
attempt was made with city illuminating gas. The possibility as to variety is great with this gas. It also failed. The resulting curves shown in fig. 6 are of the same general type as those of fig. 5, and the approximate absolute value of the limiting photoelectric current is again 250 scale-divisions. The differences in the cases of hydrogen and carbon monoxide are probably accidental since these gases are present in illuminating gas. At any rate the looked for minimum was not found. It is noted that for air and the illuminating gas, which contains traces of air, the initial photo-sensitiveness is lower than for the other gases. This indicates that the fatigue discussed in connexion with fig. 5 is to be traced to air.

These generally negative results are in direct conflict with some of those I reported in a previous paper *. It is quite evident now that the effects I once attributed to added gases are due to the remaining gases in the foil. The need of long periods of heating was not realized at the time.

Effect of Heating in Flame.

The original behaviour with respect to gases can, however, be introduced by heating in a flame. The blow-torch was allowed to play, on the part of the foil subjected to radiation, for about 15 minutes. The platinum became white hot.

Fig. 7.



After remounting and evacuating, the original curve of fig. 7 was secured. It is of the usual type, but the photo-currents are for some unknown reason smaller. The vacuum run made 20 hours later is not only of the expected type but the usual sensitiveness of 250 scale-divisions is approached at the end. The second vacuum run was made after heating with 11 amperes for 9 hours. The foil is again nearly gas-free, and the curve is like those of fig. 5 both as to type and the values of the photo-currents. The gases which disturb the photoelectric emission of platinum are shown to be introduced during the process of its preparation.

* *Loc. cit.*

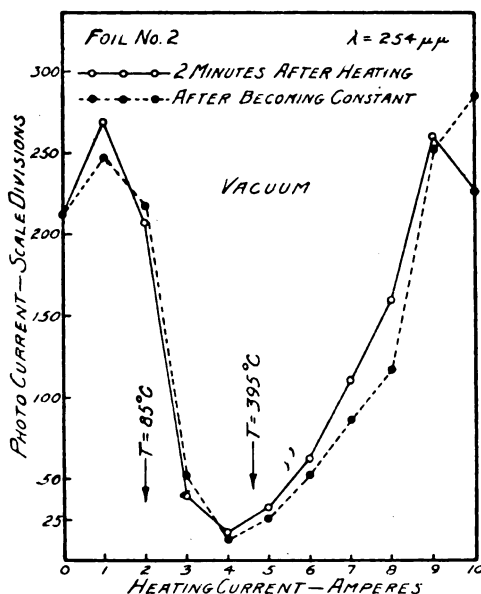
The results of this section exclude the bare possibility that the greater regularity in photo-sensitiveness shown in figs. 5 and 6 is caused by a more stable crystalline structure given to the platinum when it is heated for a long time.

The influence of water vapour has been much discussed in the literature of the photoelectric effect. The experiment was tried of letting the foil stand over-night in water vapour. A little air accidentally entered. The short curve of fig. 7 was obtained. It was not continued since its course is exactly as if the foil had stood in a vacuum or in the presence of air only.

A Small Time Effect.

It has been mentioned that when the metal becomes nearly gas-free, the photo-currents are rather unsteady after each heating. During the original run, however, and the first few repetition runs the time variation is small and has a perfectly definite direction depending on the heating-current. It was

Fig. 8.



observed that while working on the ascending part of the heating-current-photo-current curve the sensitiveness decreased after heating, but that on the descending part the sensitiveness increased. Fig. 8 gives the results of a more-

detailed study of this phenomenon. It represents an early vacuum run, so that the foil still contains much gas. The curve drawn solid is based on readings taken 2 minutes after heating. The broken curve is for readings taken after constancy is reached following each heating. The changes are proportionally small and do not affect the type of curve.

Such a vacuum run was once discontinued at the minimum at 4 amperes, and the foil allowed to remain in the vacuum until the next day. The run was again taken up, beginning with 5 amperes of heating-current. The curve duplicated those of fig. 8. Interruption of the run does not affect the type of curve. The type of curve is determined by the stage of gas elimination only and is not modified by superposed time effects.

Primary Photoelectric Effect independent of Gas Content.

Let us first consider the most likely explanation of the minima of the heating-current-photo-current curves. It has already been concluded that they are due to the absorption of the slowly moving electrons by the miniature atmosphere covering the platinum. The formation of this atmosphere at particular temperatures or heating-currents and its entire absence at others is readily conceived. The elimination of gas from a metal involves two distinct processes. In one the gas must be carried to the surface by diffusion. In the other the gas must be released from the surface. Diffusion is known to increase continually with the temperature. The release of gas is generally considered to be in the nature of a threshold phenomenon and does not become marked until particular temperatures characteristic of the system solid-gas are attained. Equilibrium between the two processes is brought about by an adjustment in the thickness or density of the layer of gas. The thickness or density thus becomes a function of the temperature, or, more specifically here, the heating-current. Take, for example, the minimum in the heating-current-photo-current curve at 4 amperes where the temperature is 290°C . On the present view the equilibrium requirement is a dense or thick layer. At succeeding heating-currents the release of gas is more rapid in proportion to the diffusion, and equilibrium is established with a thinner or less dense layer. To account for the development of a minimum beyond 10 amperes of heating-current, it is only necessary to assume the existence of another gas having a smaller temperature coefficient of

diffusion and a higher threshold temperature of release. The assumption that another disturbing gas is present is believed to be justified since the second minimum seldom appears in other than the original runs. When released it evidently comes very rapidly. Then, too, it may be present in only small amounts.

The view that has been outlined gains support from the time effects described in the preceding section. After a heating on the descending part of the curve, the accumulation of gas is greater than the equilibrium requirement as the metal cools. The gas diffuses back into the metal and the photo-current increases. On the ascending part, more gas is required for equilibrium on cooling, and it can come from the metal by diffusion or from the tube until the pumps have had time to reduce the pressure.

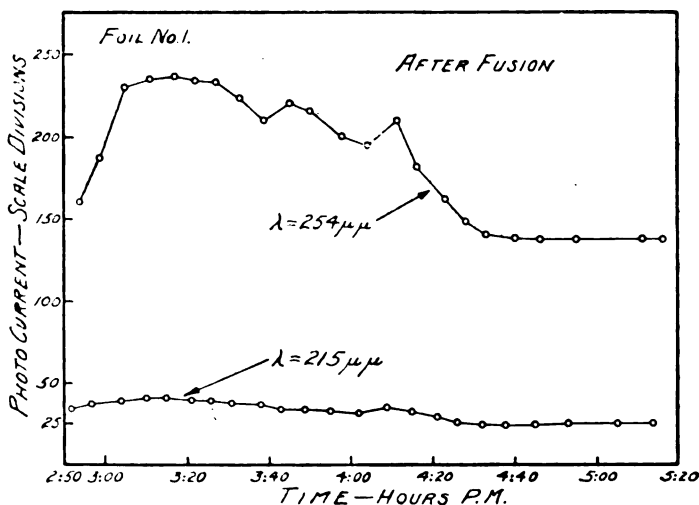
The results recently published by M. Sende and H. Simon* receive an entirely different interpretation if the foregoing view is adopted. We will direct our attention first to fig. 9 of their paper, according to which the photo-sensitiveness of platinum was reduced to $\frac{1}{60}$ of its maximum value by repeated heating at a fixed high temperature. They consider that the gas is nearly gone and that by further heating a limiting photo-sensitiveness of zero would be approached. It is most probable that their experiment was discontinued just at the stage when an absorbing layer of gas was at its greatest thickness or density in order to maintain the equilibrium between the rate of diffusion and the rate of release from the surface. A mere beginning had been made in the way of removing gases since the total time of heating was only 130×20 seconds or 43 minutes. Times of the order 9 hours were necessary in the writer's experiments. The writer believes that he could, with equal justification, extrapolate the original curves of fig. 3 of the present paper (especially for $\lambda = 254 \mu\mu$) beyond 12 amperes of heating-current and claim that the photo-electric effect of platinum vanishes when the gas is gone.

The same experimenters observed the sensitiveness of platinum immediately after fusion in a very high vacuum. It was less than $\frac{1}{1000}$ of a previous maximum value. Fig. 9 of this paper represents the writer's results in a similar experiment. The accompanying time changes are shown. The platinum was fused, after completing the runs shown in fig. 3, in a vacuum of the order 10^{-6} mm. of mercury. Although the photo-currents are smaller than the maxima shown in fig. 3

* *Loc. cit.*

they are by no means zero. At most three minutes elapsed between the time of fusion and the first measurement, so that it is not possible to extrapolate backward to zero photosensitiveness. Nor can it be said that the electrons come from the supporting iron wire behind the foil. The portion of platinum that was fused was less than a tenth of that illuminated. Moreover, the final values of the photoelectric current are smaller than the initial.

Fig. 9.



The smaller sensitiveness shown here and the close approach to zero sensitiveness in the experiment of M. Sende and H. Simon is readily explained on the theory of an absorbing layer. During fusion the increase of temperature is very sudden. If much gas remains the contribution to the surface by diffusion overwhelms the rate of release. The time of fusion is, however, too short to allow of the equilibrium adjustment to a thinner or less dense layer.

Conclusions and Summary.

The photoelectric effect in platinum has been studied as it is changed by increasing temperatures of heating in a high vacuum. The effect, measured after cooling of the metal, was plotted against the heating-current. The wave-length

limit proved to be constant, but the largest variations in sensitiveness took place with radiation of long wave-length. It is concluded that the primary emission from the platinum is constant but that an adsorbed layer of gas, whose effectiveness depends on the temperature of heating, stops the electrons of low velocity.

The evidence is considered to be in favour of the transition layer theory of adsorption and decisively against the view that the adsorbed gas consists of a single layer of molecules.

The type of curve becomes very different after the foil has been heated at as high a temperature as possible for a time of 9 hours or more. The minima of the original curves do not appear. There is always an approach to a sensitiveness of approximately 250 scale-divisions under the given experimental conditions. The sensitiveness never approaches zero. Hence the photoelectric property is primarily that of the platinum itself. The gases merely modify and always reduce the effect.

The minima of the original or repetition curves could not be reintroduced by letting the gas-free foil stand in various gases. They were reintroduced by heating with a blow-torch.

The minima of the curves are qualitatively explained in a simple manner by considering the driving off of gas as involving two distinct processes. In the first, the gas is brought to the surface by diffusion and in the second it must be released. At each heating-current or temperature, with given gas concentration in the metal, a gas layer of characteristic thickness or density brings about the equilibrium adjustment.

The experiments were performed at the Physical Institute in Uppsala. I wish to thank the Staff of the Institute and particularly its Director, Professor Gustaf Granqvist, for the aid and equipment placed at my disposal and the many courtesies shown me during my year of study in Sweden.

Physical Institute,
Uppsala, Sweden.
April 25, 1922.

LXI. *On the Theory of Generalized Quanta and the Balmer Lines.* By S. C. KAR*.

THE general principles governing the quantaic structure of phase-space were given by Planck in the *Ann. d. Phys.* vol. 50 †. This structure depends on the integrals of the motion, and in $2f$ -dimensional phase-space the elementary cell has, according to Planck, a volume equal to h^f where h is Planck's constant. Rules are also given depending on what Planck has called coherence or incoherence of coordinates which determine the splitting up of the single quantum condition respecting the volume of the cell into f different quanta conditions regarding the $f(q, p)$ -planes.

In the next volume of the *Annalen* ‡ somewhat different and simpler conditions—and these are now largely accepted—are laid down by Sommerfeld. According to Sommerfeld the elementary volume $\int dq_1 dp_1 \dots dq_f dp_f$ of phase-space may be regarded as determined by the f projections $\int dq_1 dp_1, \int dq_2 dp_2, \dots, \int dq_f dp_f$ on the $f(q, p)$ -planes. Each of these integrals is then integrated with respect to p , and then he proceeds to write

$$\begin{aligned} \int p_1 dq - \int p_0 dq &= h, \\ \int p_2 dq - \int p_1 dq &= h, \\ &\dots \dots \dots \\ \int p_n dq - \int p_{n-1} dq &= h, \\ \therefore \int (p_n - p_0) dq &= nh. \end{aligned}$$

Assuming now that of the group of curves on the (q, p) -planes a path may be obtained such that $\int p_0 dq = 0$ along it, Sommerfeld gets the simplified form $\int p_n dq = nh$. For the limits of integration he gives the rule that it should be performed over that length of the orbit which brings up fresh phases in phase-space so that in periodic orbits the integration is over one complete cycle. In Newtonian orbits of the relativistic type or other quasi-periodic orbits where there is a regular forward motion (or backward) of

* Communicated by the Author.

† *Ann. d. Phys.* vol. I. p. 385 (1916).

‡ *Ann. d. Phys.* vol. II. p. 1 (1916).

the perihelion, this means a path of integration for $\int p_r dr$ from $r_{\min}$ to $r_{\min}$ through $r_{\max}$ or, what amounts to the same, double the path from $r_{\min}$ to $r_{\max}$. For the azimuthal phase-integral $\int p_\phi d\phi$ the path is taken to be just one complete cycle of 2π and not from $r_{\min}$ to $r_{\min}$ through $r_{\max}$. The reason for this variation as given by Sommerfeld seems to be that attention should be directed not so much to the actual orbit as to its counterpart in phase-space, and since an ellipse of a given size may have any position as regards the azimuth of its perihelion, and since the whole set of such ellipses should be taken into account, all phases are comprehended in a path of integration from 0 to 2π . The results obtained from these quanta conditions taken along with Bohr's famous rule for the frequency of the emitted radiation receive startling confirmation in the experimental results of Paschen* on the Balmer lines of hydrogen. The behaviour of the Rydberg number and of doublets and triplets is sufficiently near to the requirements of the formula.

It is at once possible, however, to raise certain theoretical objections to Sommerfeld's theory. In the first place, the elementary volume $\int dq_1 dp_1 \dots dq_f dp_f$, which I take to be equal to h^f after Planck, cannot be represented as

$$\int dq_1 dp_1 \cdot \int dq_2 dp_2 \cdot \int \dots \int dq_f dp_f.$$

This objection is met partly if, on the authority of Epstein and Schwarzschild—and to this Sommerfeld agrees,—the choice of the coordinates is determined by the possibility of separation of variables in the Hamilton-Jacobi equation. If such separation can be effected we should have according to Staeckel—at least in regard to a Staude-Staeckel dynamical system— p_i a function solely of q_i . The limits for $q_1, q_2, \dots, q_f$ still remain interdependent, and this disposes of the possibility of the latter mode of representation even where the choice is made after the Epstein-Schwarzschild rule.

Secondly, the reasoning adduced by Sommerfeld in support of the path of integration for the azimuthal phase-integral $\int p_\phi d\phi$ appears to be far from convincing. It goes too far and would appear to indicate an identical path of integration for the phase-integral $\int p_r dr$. On the other hand, having in view the concepts of the time-total (Zeitgesamtheit) of phases and of the space-total (Raumgesamtheit)

* *Ann. d. Phys.* vol. 1, p. 901 *et seq.* (1916).

of phases employed in statistical mechanics and the proposition that the time-total of phases of a single orbit is equal to the space-total of phases of all similar orbits*, we should rather have the path of integration extended over the complete orbit from $r_{\min}$ to $r_{\min}$ through $r_{\max}$, seeing that although p_ϕ is constant the phase-point in phase-space does not come back to itself until starting from $r_{\min}$ we come back to $r_{\min}$ through $r_{\max}$.

A third objection to Sommerfeld's treatment of the relativistic motion is that advanced by Planck† and Schwarzschild also in regard to the azimuthal phase-integral. According to Sommerfeld himself, the integral $\int dq dp$ is reducible to the form $\int p_n dq = nh$ only where a path may be obtained such that $\int p_0 dq = 0$ along it. This, however, is not possible owing to a minimum value of the angular momentum which cannot be passed if the elliptic motion is preserved. Planck himself, in his own treatment of the relativistic motion arrives at the result $2\pi(p_n - p_0) = nh$ as the azimuthal quanta condition where p_0 is the limiting value of the angular momentum. The behaviour of the Rydberg number in the experimental results of Paschen, however, tells against the form $2\pi(p_n - p_0) = nh$.

In the present paper I shall venture to suggest a fresh standpoint in regard to quanta conditions and to develop it by reference to the particular cases of (i.) the linear oscillator, (ii.) the rotator, (iii.) the ordinary Newtonian ellipse, and (iv.) the relativistic Newtonian ellipse. While they meet all the objections stated against Sommerfeld's theory, they give results identical with those of Planck and of Sommerfeld in the first three cases. The results obtained, however, in the case of the relativistic ellipses are at variance alike with those of Sommerfeld and of Planck as well as with those which Sommerfeld would have obtained if he had taken the path of integration for the integral $\int p_\phi d\phi$ as he appears at first to have done from $r_{\min}$ to $r_{\min}$ through $r_{\max}$. The central idea in this investigation is still that of Planck, namely, the structure of phase-space must be on the basis of the integrals of the motion. As regards the experimental aspects of those conditions, I have to admit the disappearance of the doublets and the triplets; but the behaviour of the Rydberg number may be deemed to be sufficiently encouraging.

* *Repertorium der Physik*, Ganz u. Weber, p. 455.

† *Ann. d. Phys.* vol. 1. p. 404 (1916).

§ 1. *One degree of freedom. Linear oscillator, rotator.*

We may state the quantum condition in the form

$$\int_0^n \int^{\circ} dt \delta H \quad \text{or} \quad \int_0^n T \delta H = nh,$$

where H is the energy and T is the periodic time *.

(a) *Linear oscillator.*

The equation of motion is $\ddot{x} + \mu^2 x = 0$; therefore $\dot{x}^2 + \mu^2 x^2 = \text{const.} = 2H$ (twice the energy) $= \mu^2 a^2$, where a is the amplitude. $T = \frac{2\pi}{\mu}$, therefore T is independent of H , μ^2 being an absolute constant. We therefore have $T(H_n - H_0) = nh$ or if $H_0 = 0$, $TH_n = nh$. In Planck's notation ϵ_n (the energy) $= \frac{nh}{T} = nh\nu$ (where ν is the frequency).

(b) *Rotator.*

The integral of energy is $\frac{1}{2}J\omega^2 = H$ (J being the moment of inertia and ω the angular velocity). $T = \frac{2\pi}{\omega} = \frac{\pi \sqrt{2J}}{H^{\frac{1}{2}}}$; $\therefore \int_0^n T \delta H = \int_0^n \pi \sqrt{2J} \cdot 2H^{\frac{1}{2}} = nh$; if $H_0 = 0$ we have $H_n = \frac{n^2 h^2}{8\pi^2 J}$.

§ 2. *Two degrees of freedom. The ordinary Newtonian ellipse.*

We may state the quanta conditions in the forms $\int^{\circ} dt \delta H = nh$, $\int^{\circ} d\phi \delta p_{\phi} = n'h$, or in the alternative forms $\int_0^n T \delta H = nh$, and $\int_0^{n'} \Phi \delta p_{\phi} = n'h \dots$ where p_{ϕ} is the angular momentum and Φ is the azimuthal period which in the present case is 2π .

The energy $H = -E = \frac{1}{2} \left\{ m(\dot{r}^2 + r^2 \dot{\phi}^2) - \frac{2e^2}{r} \right\}$, and the angular momentum $= p = mr^2 \dot{\phi}$.

* The symbol $\int^{\circ}$ is used throughout to mean integration over a complete circuit.

The periodic time

$$T = 2 \int_{r_{\min}}^{r_{\max}} \frac{r dr}{\sqrt{\frac{2e^2}{m} r - \frac{l'^2}{m^2} - \frac{2E}{m} r^2}} = \sqrt{\frac{2m}{E}} \int_{r_1}^{r_2} \frac{r dr}{\sqrt{(r_2 - r)(r - r_1)}} \\ = \pi \sqrt{\frac{m}{2}} \frac{e^2}{E^{3/2}} [r_2 = r_{\max}, r_1 = r_{\min}].$$

Therefore

$$nh = \int_0^n T \delta H = -\pi e^2 \sqrt{\frac{m}{2}} \int_0^n \frac{\delta E}{E^{3/2}} = \pi e^2 \sqrt{2m} E_n^{-1/2};$$

therefore $H_n = -E_n = -\frac{2m\pi^2 e^4}{n^2 h^2},$

which is in perfect accord with Sommerfeld's expression $-\frac{2m\pi^2 e^4}{(n+n')^2 h^2}$ if it is noticed that the single quanta number n really absorbs n' and stands for $n+n'$.

For the azimuthal phase-integral $\int_0^{n'} \Phi \delta p$ we have $2\pi p_{n'} = n'h.$

§ 3. Theoretical considerations underlying the present mode of writing the quanta conditions.

(i.) One degree of freedom; phase-integral:—

$$\int \int \delta H = h.$$

In integrating with respect to t over the whole period it is evident that we are taking account of all phases which a particular system passes through with constant energy, and in so doing we are also taking the space-total of all phases which systems with a given energy may have in phase-space. In subsequent integration with respect to H , therefore, we are accounting for the whole of phase-space corresponding to every variation of the energy. The elementary cell in this phase-space being equal to h , we have

$$\int \int \delta H \text{ or } \int T \delta H = h.$$

(ii.) Two degrees of freedom; ordinary Newtonian

$$\text{ellipse: phase-integrals } \int \int \delta H = h; \\ \int \int \delta \phi \delta p = h.$$

What has been said respecting the case of one degree of freedom will apply equally well in this case to the phase-integral $\int \int dt \delta H$. But fresh phases come up by reason of the fact that keeping H and T constant we can vary p or the azimuth. The phases brought up by variation of azimuth have no necessary relation with those depending on time-difference, for T is a function of H while $\int d\phi$ is either an absolute constant or, as it is in the case of the relativistic ellipse, a function of p . Having regard, therefore, to the proposition that the space-total of phases of different systems having the same p , T , and H would be equal to the time-total of phases of a single system, we integrate $\int d\phi$ over the complete period. Subsequent integration with respect to p therefore accounts for all phases which can arise through these sources.

The observation may be made that the canonical coordinates $p_1 q_1, p_2 q_2$, etc. of a dynamical system are not unique and that it is easy to substitute for any pair (p, q) the pair (H, t) . It is possible therefore to represent phase-space as determined by the system of coordinates $p_2 q_2, p_3 q_3, \dots H, t$. The elementary volume of this space in the present case would be $\int d\phi \delta p dt \delta H = \int d\phi \delta p \cdot \int dt \delta H \dots$ because p and H are independent constants and Φ and T are functions of p and H respectively. This volume therefore is equal to h^2 .

§ 4. Possibility of reduction of the present quanta integrals to Sommerfeld's forms.

Writing the Hamiltonian equations of motion in the bilinear form we have $\Sigma(dq \delta p - dp \delta q) = dt \delta H$ where d refers to a variation with time and therefore along the orbit, and δ refers to a variation independent of the time. In the present case

$$(dq_r \delta p_r - dp_r \delta q_r) + dq_\phi \delta p_\phi = dt \delta H, \text{ because } dp_\phi = 0.$$

$$\text{Therefore } \delta(p_r dq_r) - d(p_r \delta q_r) + dq_\phi \delta p_\phi = dt \delta H.$$

Integrating this form over a complete cycle we have

$$\delta \left[\int p_r dq_r \right] - \left[\int p_r \delta q_r \right] + 2\pi \delta p_\phi = T \delta H^* ;$$

* The symbol $\left[\int \right]$ is used to mean the difference of values at the extremities of a complete circuit.

since $\int p_r \delta q_r$ is zero—and this may be easily verified—we may write

$$\delta \left[\int p_r dq_r \right] + 2\pi \delta p_\phi = T \delta H.$$

Integrating this equation between two orbits we have

$$\left[\int p_r dq_r \right]_1^2 + [2\pi p_\phi]_1^2 = \int_1^2 T \delta H.$$

It is now obvious that instead of associating a quanta number with the phase-integral $\int_1^2 T \delta H$ we may associate another with the integral $\left[\int p_r dq_r \right]_1^2$, which will be the difference of the quanta numbers associated with the former and with the expression $2\pi p_\phi$, and this is exactly what Sommerfeld has done.

§ 5. Case of the relativistic ellipse; phase-integrals

$$\int \dot{\phi} dt \delta H = nh, \quad \int d\phi \delta p_\phi = n'h.$$

Sommerfeld writes for the equations of motion

$$\frac{d}{dt}(m\dot{x}) = -\frac{e^2}{r} \cos \phi, \quad \frac{d}{dt}(m\dot{y}) = -\frac{e^2}{r} \sin \phi,$$

where $m = m_0 / \sqrt{1 - \beta^2}$ and $\beta = \frac{v}{c}$.

Putting $K = -m_0 c^2 \sqrt{1 - \beta^2}$ we have

$$\frac{\partial K}{\partial \dot{x}} = m\dot{x}, \quad \frac{\partial K}{\partial \dot{y}} = m\dot{y}.$$

The equations of motion are therefore deducible from $\delta \int (K - V) dt = 0$, where V is the potential $-\frac{e^2}{r}$. The angular

momentum $\frac{\partial K}{\partial \dot{\theta}} = \frac{m_0}{\sqrt{1 - \beta^2}} r^2 \dot{\theta} = m r^2 \dot{\theta} = \text{const.} = p.$

The energy

$$= \dot{x} \frac{\partial K}{\partial \dot{x}} + \dot{y} \frac{\partial K}{\partial \dot{y}} - K + V = \frac{m_0 c^2}{\sqrt{1 - \beta^2}} - \frac{e^2}{r} = H \text{ (constant).}$$

For the bilinear form of the Hamiltonian equations we proceed thus:—

$$\text{Let} \quad \int_1^2 (K - V) dt = S,$$

then

$$\delta S - \int_1^2 (K - V) \delta t = \int_1^2 \left\{ \frac{\partial K}{\partial x} (\delta x - \dot{x} \delta t) + \frac{\partial K}{\partial y} (\delta y - \dot{y} \delta t) \right\},$$

$$\text{therefore} \quad \delta S = \int_1^2 (\Sigma p \delta q - H \delta t).$$

If d is a variation with time and therefore along the orbit, we have easily

$$(dq_r \delta p_r - dp_r \delta q_r) + dq_\phi \delta p_\phi = dt \delta H,$$

$$\text{i. e.} \quad \delta(p_r dq_r) - d(p_r \delta q_r) + dq_\phi \delta p_\phi = dt \delta H.$$

Now the differential equation of the orbit has been deduced by Sommerfeld in the form

$$\frac{\partial^2 \sigma}{\partial \phi^2} + \sigma \left\{ 1 - \frac{e^4}{p^2 c^2} \right\} = \frac{m_0 e^2}{p^2} \left\{ 1 + \frac{H}{m_0 c^2} \right\},$$

and the equation to the orbit in the form $\sigma = A(1 + \epsilon \cos \gamma \phi)$,

$$\text{where } \sigma = \frac{1}{r}, \quad A = \frac{m_0 e^2}{p^2 \gamma^2} \left(1 + \frac{H}{m_0 c^2} \right), \quad \gamma^2 = 1 - \frac{e^4}{p^2 c^2}.$$

ϵ is given by the relation which is easily deduced,

$$1 + \frac{H}{m_0 c^2} = \sqrt{\frac{p^2 - p_0^2}{p^2 - \epsilon^2 p_0^2}}, \quad \text{where } p_0 = \frac{e^2}{c}.$$

The azimuthal period $= \frac{2\pi}{\gamma}$; therefore the phase-integral

$$\begin{aligned} \int_0^n \int_0^{\bar{0}} dq_\phi \delta p_\phi \\ = \int_0^{n'} \frac{2\pi}{\gamma} \delta p = 2\pi \int_0^{n'} \frac{p \delta p}{\sqrt{p^2 - p_0^2}} = 2\pi \left[\int_0^{n'} \sqrt{p^2 - p_0^2} \right], \end{aligned}$$

$$\therefore \quad 2\pi \sqrt{p^2 - p_0^2} = n' h.$$

For the phase integral $\int_0^n \int_0^{\bar{0}} dt \delta H$ we integrate the bilinear form over the whole orbit and obtain

$$T \delta H = \delta [\int_0^{\bar{0}} p_r dq_r] - [\int_0^{\bar{0}} p_r \delta q_r] + \frac{2\pi}{\gamma} \delta p.$$

But
$$[p_r, \delta q_r] = \left[\frac{p}{m_0 \sigma^2} \sqrt{1 - \beta^2} \frac{\partial \sigma}{\partial \phi} \left\{ - \frac{\delta A}{A^2 (1 + \epsilon \cos \gamma \phi)} - \frac{\delta \epsilon \cos \gamma \phi}{A (1 + \epsilon \cos \gamma \phi)^2} + \frac{\epsilon \sin \gamma \phi}{A (1 + \epsilon \cos \gamma \phi)^2} \cdot \phi \cdot \delta \gamma \right\} \right]_0^{2\pi} = 0.$$

Therefore
$$T \delta H = \delta \left[\int p_r dq_r + 2\pi \sqrt{p^2 - p_0^2} \right],$$

which shows that $T \delta H$ is an exact differential and T is a function solely of H .

Sommerfeld evaluates

$$\int p_r dq_r = 2\pi \sqrt{p^2 - p_0^2} \cdot \left\{ \frac{1}{\sqrt{1 - \epsilon^2}} - 1 \right\}.$$

Therefore
$$T \delta H = \delta \left[2\pi \sqrt{\frac{p^2 - p_0^2}{1 - \epsilon^2}} \right].$$

But
$$1 + \frac{H}{m_0 c^2} = \sqrt{\frac{p^2 - p_0^2}{p^2 - \epsilon^2 p_0^2}} = \sqrt{s} \text{ (say),}$$

from which we obtain
$$\frac{p^2 - p_0^2}{1 - \epsilon^2} = \frac{s p_0^2}{1 - s}.$$

Therefore

$$\int_0^n T \delta H = 2\pi \left(\frac{s_n p_0^2}{1 - s_n} \right)^{\frac{1}{2}} = nh \text{ (} s_0 = 0, \text{ for the zero path),}$$

or
$$1 + \frac{H_n}{m_0 c^2} = \frac{nh}{\sqrt{n^2 h^2 + 4\pi^2 p_0^2}}.$$

It will be seen that the energy thus depends on a single quanta number, and the doublets and triplets of the Balmer series would receive no explanation.

§ 6. Comparison with the quanta propositions of Planck and Sommerfeld.

Sommerfeld writes

$$2\pi \sqrt{p^2 - p_0^2} \left\{ \frac{1}{\sqrt{1 - \epsilon^2}} - 1 \right\} = nh \quad \text{and} \quad 2\pi p = n'h,$$

while with Planck the latter would stand in the form

$$2\pi(p - p_0) = n'h.$$

According to Sommerfeld's original view of the path of integration for the azimuthal phase-integral the latter would stand in the form

$$\frac{2\pi p^2}{\sqrt{p^2 - p_0^2}} = n'h.$$

All the azimuthal relations are therefore different from the relation $2\pi \sqrt{p^2 - p_0^2} = n'h$ proposed in this paper, while if the present relation is admitted then the radial quanta number of Sommerfeld would appear to be the difference of the quanta numbers associated with the time-energy integral and with the azimuthal integral.

It is also obvious that

$$\int d\phi \delta p dt \delta H = \int d\phi \delta p \cdot \int dt \delta H,$$

since the period in ϕ is a function entirely of p , and the period in t that of H . Thus the elementary cell in phase-space has a volume equal to h^2 . It will also appear that the least value of p , which is p_0 , cannot be passed in quanta changes.

§ 7. *Comparison with Paschen's experimental results on the behaviour of the Rydberg number in the Balmer Series.*

We have
$$\frac{H_n}{m_0 c^2} = \frac{nh}{\sqrt{n^2 h^2 + 4\pi^2 \frac{e^4}{c^2}}} - 1.$$

But $e = 4.7 \cdot 10^{-10}$; $h = 6.5 \cdot 10^{-27}$; $c = 3 \cdot 10^{10}$

therefore $\frac{4\pi^2 e^4}{c^2 h^2}$ is of the order of 10^{-3} .

Therefore

$$\begin{aligned} \frac{H_n}{m_0 c^2} &= \frac{1}{\left(1 + \frac{4\pi^2 e^4}{c^2 n^2 h^2}\right)^{\frac{1}{2}}} - 1 \\ &= -\frac{2\pi^2 e^4}{c^2 n^2 h^2} + \frac{6\pi^4 e^8}{c^4 n^4 h^4} - \text{etc}; \end{aligned}$$

therefore

$$\begin{aligned}\frac{1}{\lambda} &= \frac{\nu}{c} = \frac{H_n - H_{n'}}{ch} \\ &= \frac{2\pi^2 e^4 m_0}{ch^3} \left(\frac{1}{n'^2} - \frac{1}{n^2} \right) \left\{ 1 - \frac{3\pi^2 e^4}{c^2 h^2} \left(\frac{1}{n^2} + \frac{1}{n'^2} \right) + \dots \right\} \\ &= N \left(\frac{1}{n'^2} - \frac{1}{n^2} \right) \left\{ 1 - \frac{3\pi^2 e^4}{c^2 h^2} \left(\frac{1}{n^2} + \frac{1}{n'^2} \right) + \dots \right\},\end{aligned}$$

where N is the Rydberg number.

The corrected Rydberg number N' therefore for the hydrogen lines

$$= N \left\{ 1 - \frac{3\pi^2 e^4}{c^2 h^2} \left(\frac{1}{2^2} + \frac{1}{n^2} \right) \right\}.$$

According to Sommerfeld

$$N' = N \left\{ 1 + \frac{\pi^2 e^4}{c^2 h^2} \left(\frac{1}{2^2} + \frac{1}{n^2} \right) \right\}.$$

It will thus appear that the order of the correction here proposed, unlike that suggested by Planck, agrees with that of Sommerfeld's formula. There is however a difference in sign. However, if we observe Paschen's experimental values for H_α , H_β , H_γ , H_δ , which are as follow * :

$$\begin{array}{cccc} H_\alpha & H_\beta & H_\gamma & H_\delta \\ N' \mid 109678 \cdot 205 \mid 109678 \cdot 164 \mid 109678 \cdot 167 \mid 109678 \cdot 198 \mid , \end{array}$$

it will be noticed that apart from H_α the successive numbers show an increase and not a decrease, and this fact is in harmony with the formula here proposed rather than with Sommerfeld's form which by making ΔN positive would cause N to decrease down the series.

§ 8. Conclusion.

The extension of the theory of the present paper to a case of n degrees of freedom may be made provided we have the n first-integrals of the motion of which one is necessarily the integral of energy. When the positional coordinates, which are canonical conjugates of the integration-constants treated

* *Ann. d. Phys.* vol. 1. p. 935 (1916).

as momenta, are obtained, the quanta-integrals may be written in the forms

$$\int_0^n T \delta H = nh, \quad \int_0^{n'} \Phi \delta p_\phi = n'h, \quad \int_0^{n''} \Psi \delta p_\psi = n''h, \text{ etc.,}$$

T , Φ , Ψ , etc. being the periods of the system with respect to such positional coordinates.

It is evident that a quanta integral would tend to become infinite if the periodic time or the period of the positional coordinate is infinite, *i. e.* if the dynamical system in respect of that particular coordinate is not periodic. It would thus follow that quantaic changes of energy or momenta are a property of periodic or quasi-periodic motions and that where there is no periodicity the energy changes or momenta changes must be gradual—a fact which will ensure a finite value for the quanta-integral.

Summary.

In this paper the suggestion has been made on theoretical grounds of statistics that the quanta integral in the case of one degree of freedom should be written in the form

$$\int_0^n T \delta H = nh,$$

and that in the case of Newtonian elliptic motion both of the ordinary and the relativistic type quanta integrals should be written in the forms

$$\int_0^n T \delta H = nh, \quad \int_0^{n'} \Phi \delta p = n'h$$

(where T is the periodic time, H the energy, Φ the complete azimuthal period, and p the angular momentum). The consequences of this theory are compared with those of Sommerfeld's and with the observations of Paschen on the Balmer lines of hydrogen, and it is shown that while the doublets and triplets receive no direct explanation, there being no splitting of energy as with Sommerfeld, the behaviour of the Rydberg number may be regarded as somewhat more satisfactory.

LXII. The Meaning of "a" and "b" in the Equation of State. By ANGUS F. CORE, *Chemical Department, University of Manchester* *.

IN the second part of a paper entitled "Notes on the Kinetic Theory of Gases" (Phil. Mag., May 1922) Mr. Fowler calculates the value of van der Waals' "a." There seems to me to be something unsatisfactory in taking the "a" that he finds to correspond to the "a" of van der Waals' equation of state. This equation may be written in the form

$$pv = RT + RTb/v - a/v$$

when the gas is moderately rarefied. The general virial equation so far as the second virial term is $pv = RT + B/v$. Now except under certain conditions, even when the molecules contain perfectly hard kernels, the term B/v does not naturally fall into two parts corresponding to RTb/v and a/v , that is into two parts one of which is proportional to the temperature and the other independent of the temperature. Therefore, in order to separate B/v into two parts it is necessary to define either "a" or "b."

When the molecules have perfectly hard kernels, then RTb/v may be defined as that part of the virial due to the forces that arise when the kernels actually collide. If σ is the diameter of the kernels and $-\chi(\sigma)$ the work required to separate to infinity two molecules in contact, then, as Reinganum showed, this collision virial equals

$$\frac{2\pi N\sigma^3}{3v} e^{-\frac{\chi(\sigma)}{kT}}.$$

The rest of the virial

$$\frac{B}{v} - \frac{2\pi N\sigma^3}{3v} e^{-\frac{\chi(\sigma)}{kT}},$$

may be called $-a/v$, but this does not mean that the "a" so defined corresponds satisfactorily with the "a" of van der Waals.

B/v can, however, be separated into two parts by defining the meaning of "a." Thus a/v may be defined as half the work required to abstract N molecules chosen at random from the interior of the gas to infinity outside the gas. This definition is, however, ambiguous. The ambiguity is removed by stating that when a molecule is being removed the other molecules are to be considered fixed in position.

* Communicated by Prof. A. W. Porter, F.R.S.

The work done on a molecule then gives the change in the potential of the molecule usually referred to as χ ; and the work for the N molecules will give the increase in potential energy consequent on the removal of one gram molecule from the interior of a vessel filled with the gas. Minus half this quantity, that is $-a/v$, is the potential energy of a gram molecule of the gas. To the same degree of approximation as results from the neglect of all the virial terms beyond the second, "a" is independent of v . Therefore

$$\frac{a}{v} = -v \frac{d \frac{a}{v}}{dv}.$$

According to the classical kinetic theory the kinetic energy is constant so long as the temperature is constant, so that if U is the total energy of the gas per gram molecule

$$\frac{a}{v} = v \left(\frac{\partial U}{\partial v} \right)_T.$$

Therefore

$$\frac{a}{v} = v \left(T \left(\frac{\partial p}{\partial T} \right)_v - p \right).$$

This allows a/v to be calculated when the equation of state is known. Expressed directly in terms of the molecular field, the potential energy per gram molecule is given by

$$-\frac{a}{v} = \frac{2\pi N^2}{v} \int_0^\infty r^2 \chi e^{-\frac{\chi}{kT}} dr$$

in which χ is the potential of a molecule at a distance r from the centre of another molecule.

It is the a/v thus defined that corresponds most closely with the a/v of the equation of van der Waals. The remaining part of the second virial term may be called RTb/v . This cannot be called the collision virial, for when the molecules contain a hard kernel it does not in general reduce to the collision virial of Reinganum. Perhaps the best name for the two parts of the second virial term as defined above are the potential part and the non-potential part.

a/v may, however, be defined as half the work required to remove N molecules chosen at random when, during the removal, the other molecules are allowed to move into their new positions of statistical equilibrium, the volume of the gas being kept constant. This work does not equal the increase

624 *Meaning of "a" and "b" in the Equation of State.*

of potential energy, and is usually less. If carried out under isothermal conditions there will be an exchange of heat with the surroundings. When the gas is sufficiently rarefied so that the variation in density towards the boundary can be neglected, then $-a/v$ thus defined must equal the entire term B/v .

When the molecules contain a hard kernel we may modify this definition of a/v by excluding from this term that part of the work done by the impulse forces arising on collision. This, in effect, is what Mr. Fowler does. But even then this remaining work does not give the increase in potential energy consequent on the removal of the molecules.

The division of the term B/v which follows from this definition of a/v must be the same as that of Reinganum, for the other part of the term—that is RTb/v , is due to the collision impulses.

This method of division, apart from the fact that it is only applicable when the kernels are perfectly hard, may give rise to a separation which has very little significance. Suppose, for example, that the field of the molecule consists of an inner spherical region of radius σ throughout which the potential is infinite, surrounded by a shell of thickness d across which the potential rises from $\chi(\sigma)$ on the surface just outside the inner region to zero on the outer surface. The collision virial is equal to

$$\frac{2\pi N\sigma^3}{3v} e^{-\frac{\chi(\sigma)}{kT}},$$

whatever be the value of d . If d is made indefinitely small the total virial must be $\frac{2\pi N\sigma^3}{3v}$, for the molecules are indistinguishable from simple hard spheres of diameter σ . Therefore, if we insist on making the collision virial correspond to RTb/v , the value of a/v must be

$$\frac{2\pi N\sigma^3}{3v} \left(e^{-\frac{\chi(\sigma)}{kT}} - 1 \right).$$

But it is evident that, the molecule now being a hard sphere without external field, the proper value of the a/v of van der Waals is 0, and that of RTb/v is $\frac{2\pi N\sigma^3}{3v}$.

The University, Manchester,
September 1922.

LXIII. *On the Molecular Scattering and Extinction of Light in Liquids and the Determination of the Avogadro Constant.*
By C. V. RAMAN, M.A., Hon. D.Sc., Palit Professor of Physics in the Calcutta University, and K. SESHAGIRI RAO, M.A., University of Madras Research Scholar*.

1. Introduction.

THE phenomena of molecular scattering of light in liquids are of great interest from several different points of view. Apart from the importance they possess as an illustration of optical theory, their study throws light on fundamental problems concerning the nature of the liquid state and the anisotropic structure of atoms and molecules. They are also concerned in the explanation of one of the most beautiful of natural phenomena, that is, the colour of the deep sea and of other large masses of clear water, as has been explained by one of us in a recently published book †. It may also be pointed out that the molecular scattering of light in the oceanic waters contributes in a noticeable degree to the albedo of the earth and thus possesses an astronomical significance. It is proposed in this paper to discuss in detail the theory of molecular diffraction in liquids and to describe further experimental work on the subject.

2. Einstein-Smoluchowski Formula.

A suggestion has been made by some previous writers ‡ that the Rayleigh law of scattering according to which the fraction of the incident energy that is laterally scattered in passing through a unit volume of the substance is

$$\frac{32\pi^3(\mu-1)^2}{3n\lambda^4}, \quad (1)$$

applies also to liquids. *This is not true.* The assumption on which the law of scattering stated in (1) is derived, namely, that the scattered waves arising from the individual molecules arrive in arbitrary phases at the point of observation, is certainly not applicable in the case of condensed media, as

* Communicated by the Authors.

† 'Molecular Diffraction of Light,' Calcutta University Press, February 1922. See also 'Nature,' Nov. 24, 1921, and "The Molecular Scattering of Light in Water and the Colour of the Sea," Proc. Roy. Soc. April 1922.

‡ F. E. Fowle, *Astrophysical Journal*, vol. xxxviii. p. 392 (1913); Cabannes, *Ann. de Phys.* tome xv. pp. 1-150 (1920).

Phil. Mag. S. 6. Vol. 45. No. 267. March 1923. 2 S

was indeed pointed out by the late Lord Rayleigh himself. The molecules in such a media are within each other's sphere of action practically all the time, and their ordering in space is therefore very far indeed from being a random arrangement. The relative phases of the scattered waves from the individual molecules are hence not uncorrelated, and we cannot expect the fraction of the incident energy which appears as scattered light to be given by (1).

A more promising method of approach for dealing with the problem of molecular scattering of light in liquids is the "Theory of Fluctuations" developed by Einstein and Smoluchowski, of which a discussion has been given in the paper on molecular scattering in dense vapours and gases*. According to this theory, the fraction of the incident energy which is scattered in passing through unit volume of fluid is

$$\frac{8\pi^3 RT\beta(\mu^2 - 1)^2(\mu^2 + 2)^2}{27N\lambda^4}, \quad . \quad . \quad . \quad (2)$$

where β and μ are respectively the compressibility and refractive index of the fluid, T is the absolute temperature, λ is the wave-length of the incident light, R is the gas-constant, and N the Avogadro number, both the latter referring to a gram-molecule. According to this theory, the light scattered by a liquid in a direction transverse to the primary beam should be completely polarized. It has been already pointed out by one of us† that the intensity of the transversely scattered light is correctly given by the Einstein-Smoluchowski formula in the case of those liquids in which its polarization is tolerably complete. In the case of many liquids, however, a very considerable admixture of unpolarized light appears, and we have now to consider the explanation of this fact and the modification of the theory that it necessitates.

3. *Imperfect Polarization of Transversely Scattered Light in Liquids.*

As already explained in the paper on scattering in dense vapours and gases, the Einstein-Smoluchowski theory is based on purely thermodynamic conceptions and practically does not consider the molecular structure of the fluid at all. It, in fact, regards a fluid as a continuous medium which is, however, subject to local fluctuations of density, and makes

* C. V. Raman and K. R. Ramanathan, *Phil. Mag.* January 1923.

† *Loc. cit.*

use of the Lorentz-Mosotti relation connecting changes of refractive index with the density to evaluate the intensity of the scattered light. If, however, we consider the subject from a molecular standpoint, the same result as that contained in the Einstein-Smoluchowski formula would be obtained, provided it be assumed that the molecules are isotropic. In the general case of a liquid consisting of anisotropic molecules, we may divide the effect to be expected into two parts: (*a*) a part due to the thermal fluctuations of density, and (*b*) a part due to the anisotropy and varying orientations of the molecules. We may assume without appreciable error that part (*a*) would be quantitatively determined by the Einstein-Smoluchowski theory, and that this part of the scattered light observed transversely to the primary beam would be completely polarized. From general considerations it would appear that part (*b*) should consist almost entirely of unpolarized light having an equal intensity in all directions. For, in an ordinary liquid, the molecules do not tend to set themselves definitely in any particular direction, and though in the case of molecules possessing permanent electrical or magnetic moments, a mutually directive influence may be perceptible, the molecules in any appreciable volume of the liquid find themselves, on the average, in all possible orientations relatively to the direction of the incident light vector. Hence the light vector in part (*b*) lies mostly in all possible orientations. However, to be quite accurate, we may assume that part (*b*) also includes a certain proportion of polarized light, and proceed to find the increase resulting therefrom in the intensity of the transversely scattered light. Assuming the incident and scattered beams to lie in a horizontal plane and the former to be unpolarized, we may write down the expressions for the intensity of the vertical and horizontal components in the scattered beam. The intensity of the vertical component is $\Omega_0 + \epsilon\Omega_1 + 2\Omega_1$ and of the horizontal component is $2\Omega_1$, where Ω_0 is the contribution arising from density fluctuations and Ω_1 that arising from molecular anisotropy, of which the polarized part $\epsilon\Omega_1$ appears only in the vertical component. The unpolarized part Ω_1 appearing both in the horizontal and vertical components is multiplied by the factor 2 in each case as it arises in equal proportions from the vertical and horizontal components of the *incident light*.

The ratio of the intensities of the horizontal and the vertical components is thus

$$\frac{2\Omega_1}{\Omega_0 + \epsilon\Omega_1 + 2\Omega_1} = \rho \text{ (say),} \quad \quad (3)$$

628 Prof. C. V. Raman and Mr. K. S. Rao on *Molecular*
and the total intensity is

$$\Omega_0 + \epsilon\Omega_1 + 4\Omega_2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

which may be written in the form

$$\Omega_0 \cdot \frac{6+6\rho}{6-(6+3\epsilon)\rho} \cdot . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The intensity of the light transversely scattered is thus greater than that indicated by the Einstein-Smoluchowski formula in the ratio

$$\frac{6+6\rho}{6-(6+3\epsilon)\rho} \cdot . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

We have now to determine the values of ρ and ϵ in the case of liquids. The case of gases with anisotropic (ellipsoidal) molecules has been investigated by the late Lord Rayleigh, who has shown that if A, B, C are three parameters expressing the light-scattering power of a molecule for three mutually perpendicular directions of vibration fixed in it, the ratio of the intensities of the weaker and stronger components of the transversely scattered light is

$$\rho = \frac{2(A^2 + B^2 + C^2 - AB - BC - CA)}{4(A^2 + B^2 + C^2) + AB + BC + CA} \cdot . \quad . \quad (7)$$

The total intensity is proportional to

$$\frac{1}{15} [6(A^2 + B^2 + C^2) - (AB + BC + CA)]. \quad . \quad . \quad (8)$$

Since $(\mu-1)^2$ for the gas is proportional to $(A+B+C)^2$, it may easily be shown by eliminating A, B, and C with the aid of (7), as has been done by Cabannes, that the actual intensity of scattering given by (8) is greater than for a gas of equal refractivity having isotropic molecules in the ratio

$$\frac{6(1+\rho)}{6-7\rho} \cdot . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

In order that our formula (6) may be applicable generally (that is, both for liquids and gases) it must reduce to (9) in the case of gases, and this will be so provided $\epsilon = \frac{1}{3}$. This value of ϵ (that is, the proportion of polarized to unpolarized light in the additional scattering due to molecular anisotropy) agrees with the result of an investigation by Born* for the cases of gases with anisotropic molecules, and since,

* *Verh. Deutsch. Phys. Gesell.* vol. xix. p. 243 (1917); vol. xx. p. 16 (1918).

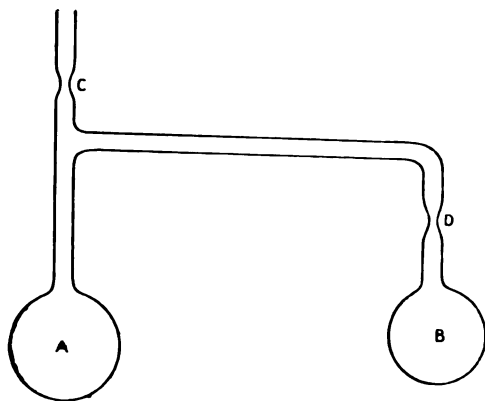
in any event, its influence is small, as may be seen from (4), we may at least tentatively take $\epsilon = \frac{1}{2}$ generally. The actual intensity of transverse scattering is thus greater than the scattering given by the Einstein-Smoluchowski formula in the ratio $\frac{6(1+\rho)}{6-7\rho}$. We shall refer to this multiplying factor in future as the Cabannes correction. The value of ρ , as can be seen from (3) and (4), depends on the relative magnitudes of Ω_0 and Ω_1 , that is, on the relative importance of density fluctuations and of anisotropy in the total light-scattering, and will thus vary considerably with the condition of the substance. In a gas obeying Boyle's law, both the position and orientations of the molecules may be taken to be absolutely at random, and the intensity of both types of scattering is in proportion to the density of the gas. The state of polarization of the light scattered by a gas or vapour obeying Boyle's law does not therefore depend on its density or temperature. The case is, however, altered when the conditions are such that there are considerable deviations from Boyle's law, or when the substance is in the state of liquid. *In liquids under ordinary conditions*, owing to the very small value of the compressibility, the scattering due to density fluctuations is considerably less than in proportion to the density of the liquid. The scattering due to the anisotropy of the molecules, on the other hand, would be simply proportional to the number of molecules per unit volume: that is, to the density, *provided we assume that in the liquid state the molecules are oriented at random and their mutually directive influences do not exercise any sensible effect*. It follows from (3) that the proportion of the unpolarized to the polarized part in the light scattered by a liquid would therefore be much greater than for the same substance in the condition of vapour at ordinary pressure. The state of affairs, on the other hand, is reversed when we consider a liquid at higher temperatures and pressures approaching the critical condition, when the scattering power given by the Einstein-Smoluchowski formula is *greater* than in proportion to the density. The ratio of the unpolarized to the polarized part would then be *smaller* than for vapours at ordinary pressures. In any case, the percentage of unpolarized light may be calculated theoretically for any arbitrary condition of temperature and pressure on the basis of the assumption referred to, when it is known for one particular case, *e.g.*, for the state of rarefied vapour. In the case of a gas or vapour the maximum value of ρ is $\frac{1}{2}$, corresponding to the case of a linear molecule. In the case of a

liquid the maximum value of ρ is $\frac{2}{3}$, which is only reached when the scattering due to density fluctuations is altogether negligible in comparison with that due to orientation fluctuations. If $\epsilon=0$, then ρ may have any value up to unity.

4. *Observations of Light Scattering in Liquids.*

In the paper on "The Colour of the Sea"*, some observations on the intensity and polarization of comparatively mote-free water obtained by simple distillation and settling have already been described. For a more careful quantitative examination, liquids purified by repeated slow distillations *in vacuo* may be used. A convenient form of apparatus for this purpose has been described by W. H. Martin†. A bulb of the form shown in fig. 1 may be used.

Fig. 1.



A quantity of the pure liquid under examination is introduced through C into the bulb A, and the vessel is then exhausted and sealed off at C. Warming up A a little and lowering the temperature of B, the liquid distils over into the latter, and in order to cleanse it thoroughly, the distillate is rinsed back into A several times. The fourth or fifth distillate, if considered satisfactory, is retained in the bulb B, which is then sealed off at D and detached. If the bulb

* Proc. Roy. Soc. April 1922; see also 'Molecular Diffraction of Light,' *loc. cit.*

† Journal of Physical Chemistry, xxiv. (1920) p. 478 and Jan. 1922.

be now placed in the path of a narrow cone of sunlight from a condensing lens which is focussed at its centre, the brilliant blue track of the beam in the liquid can be easily seen. In order to avoid the effect of stray light reflected from the sides of the bulb, it may be painted dead black outside, or in the alternative be immersed in a large beaker containing clear distilled water, which is painted dead black outside, openings being left for admission and exit of the beam and observation of the scattered cone of light passing through the liquid. The intensities of the scattered light from different liquids may be accurately compared with each other or with that in ether vapour saturated at room-temperature by a photographic method. The tracks are photographed side by side with equal exposures on a plate, the aperture of the camera-lens being varied by trial so as to obtain a record with the same degree of blackening. The ratio of the apertures gives immediately the ratio of the intensities. Since the scattering power of ether vapour at ordinary temperature is known absolutely from the experiments of Lord Rayleigh, the observations enable a comparison to be made of the scattering power of the liquid with the theoretical value indicated by the Einstein-Smoluchowski formula with the Cabannes correction.

The degree of polarization of the scattered light may be easily determined visually with the aid of a double-image prism and a nicol. The double-image prism gives two images of the track polarized respectively in horizontal and vertical planes, and by rotating the nicol placed behind it, two positions may be found in which the images appear of equal intensity. If 2θ be the angle between these two positions of the nicol, then, obviously, $\rho = \tan^2 \theta$. By inserting in the path of the cone of the sunlight before it enters the bulb one or other of a succession of Wratten colour filters transmitting restricted regions of the spectrum, the dependence of the degree of polarization on the wavelength of the scattered light has been studied.

5. Some Experimental Results.

The results shown in Table I. illustrate the agreement of the observed light scattering power of liquids with that calculated from the theoretical considerations set out in articles 2 and 3. The observed data relate to the integrated effect of the whole spectrum when colour filters were not used.

TABLE I.

Liquid.	Mean refractive index μ .	Compressibility $\beta \times 10^6$ per atmosphere.	$\rho = \frac{\text{weak comp.}}{\text{strong comp. of polarization.}}$	Obannes factor $\frac{6(1+\rho)}{6-7\rho}$.	Observed scattering power in terms of pure air at N.T.P.	Calc. value.
			Per cent.			
Water	1.337	42	12.5	1.30	165	177
Ether.....	1.358	200	8.3	1.19	860	926
Methyl alcohol }	1.333	130	15.1	1.39	495	560
Ethyl alcohol }	1.366	120	13.0	1.33	620	653
Benzene	1.510	100	39.8	2.62	3135	2861
Chloroform ...	1.450	145	15.0	1.39	1567	1503
Carbon tetrachloride }	1.467	100	11.0	1.27	1040	1056
Toluene	1.510	110	40.0	2.73	2970	3146
Carbon bisulphide } ...	1.650	104	70.0	9.27	16000	23120

The general agreement is satisfactory, any discrepancies noted being in all probability due to uncertainty in the value of the compressibility β of the liquid, except in the case of carbon disulphide for which we get a better result if in (3) and (4) ϵ is taken as zero.

6. *Dependence of Polarization and Intensity on the Frequency of the Light.*

In several liquids studied, a distinct dependence of the value of ρ (the ratio of the weak to the strong component of polarization) on the frequency of light was found. The results are shown in Table II.

This observed dependence of the state of polarization of the scattered light on its frequency is very important, as it indicates that the molecular anisotropy indicated by the experiment is connected with the optical resonance frequencies of the molecules.

The dependence of the intensity of the scattered light on the frequency is determined by three factors. The first is the λ^{-4} law, which is obviously the most important and determines the blue colour of the scattered light. Then again the refractive index μ of the liquid which appears in

the formula is not independent of the wave-length, and in the case of highly dispersive liquids, its variation would not have a negligible influence. Finally, since ρ depends on the wave-length, the Cabannes correction which, as we have seen,

TABLE II.
 ρ expressed in percentages.

Liquid.	Mean value of ρ for whole spectrum.	Value of ρ .				
		Red.	Yellow.	Green.	Blue.	Violet.
Water ...	Per cent. 12.5	9.4	10.6	10.7	15.5	21.0
Ether	8.3	8.2	8.2	8.2	9.0	9.2
Methyl alcohol }	15.1	12.5	12.6	12.6	15.0	17.2
Ethyl alcohol }	13.0	10.9	10.9	10.9	13.0	15.0
Benzene ...	39.8	39.8	39.8	39.8	41.0	41.0
Toluene ...	40.0	40.0	40.0	40.0	40.0	40.0

is of great importance in the case of liquids, would vary with the frequency in a manner characteristic of the liquid. Thus we cannot expect the ratio of intensities of the scattered light to the incident light to vary exactly in inverse proportion to the fourth power of the wave-length. This is no doubt the explanation of the fact that the colours of the track of the primary beam in different liquids do not exactly match each other, even when the intensities are equalized by altering the apertures.

7. Dependence of Intensity and Polarization on Temperature.

From the Einstein-Smoluchowski formula, it is clear that the scattering power of a fluid is proportional to the absolute temperature T , and it is also influenced by the changes of the refractive index and the compressibility β , which are both functions of temperature. In general, as the temperature rises, the density and therefore also the refractive index diminishes and the compressibility increases. The influence of the latter usually preponderates, with the result that increase of temperature generally means a considerable increase in the scattering power of the liquid. In special

cases, *e. g.*, water, where the compressibility shows a fall with rising temperature, a moderate increase of temperature should not produce much effect, but ultimately here as well a sufficient increase of temperature must result in an increased scattering. As the critical temperature of the substance is approached, the compressibility increases rapidly and ultimately becomes very large, and the scattering in the liquid becomes very great, giving rise to the well-known opalescence observed under the critical conditions. This increase in scattering may be very readily observed by putting the liquid in a strong sealed bulb and placing it in an enclosed electrical heater provided with suitable windows for ingress and egress of the illuminating pencil and for observation of the scattered light. Studies of this kind have been carried out by other workers in the author's laboratory for a number of liquids (ether, benzene, pentane, etc.) over a large range of temperatures, and the results together with a discussion are being published in separate papers. In the case of liquid ether, the increase in scattering with the rise and its decrease with the fall of temperature may easily be demonstrated by immersing the bulb in a beaker of hot water or in a Dewar flask containing a suitable cooled liquid. As an instance of the effects observed may be mentioned some measurements made with ether at 0°C . and 60°C . The ratio of the scattering powers at these temperatures was observed and found to be 1.60. The compressibility increases from 160×10^{-6} to 300×10^{-6} and the refractive index falls from 1.370 to 1.334, and the ratio of the scattering powers at these temperatures indicated by the Einstein-Smoluchowski formula is 1.41, showing a fair agreement with observation.

It is important to notice that the state of polarization of the scattered light also alters considerably with change of temperature. The quantity ρ and the Cabannes factor $\frac{6(1+\rho)}{6-7\rho}$ are thus both functions of temperature. That this is to be expected has already been pointed out in Art. 3, inasmuch as the scattering Ω_0 due to density fluctuations follows the Einstein-Smoluchowski formula and thus increases with rise of temperature, while the scattering $\frac{13}{3}\Omega_1$ due to anisotropy should (on the assumption of purely random orientation of the molecules) be proportional to the density, and thus actually diminish with the fall of temperature. Actually, by working with sealed tubes, the changes in the polarization of the light scattered both by liquids and

by vapours have been studied, and it has been found in general agreement with the theory that the polarization becomes more and more nearly perfect as the critical temperature is approached. It does not fall within the scope of this paper to go more fully into the experimental details on this point, but it is worth while here to draw attention to the question how far the relation between the value of ρ for the vapour and for the liquid obtained on the assumption that the molecules are oriented absolutely at random in both cases, and that the mutual *orienting* influence of the molecules is negligible, is in agreement with facts.

TABLE III.
 ρ is expressed in percentages.

Liquid.	Observed value of ρ in vapour.		Calc. value of ρ for liquid.	Obs. value of ρ for liquid.
	Rayleigh.	Authors.		
Ether	1.7	1.7	Per cent. 10.9	Per cent. 8.3
Benzene	6.0	7.0	40.0	39.8
Chloroform ...	3.0	3.0	18.2	15.0
Carbon tetrachloride } ...	3.2	3.0	27.7	11.0
Carbon bisulphide } ...	12.0	?	45.0	70.0

The values of ρ in the state of vapour for the substances shown in Table III. have been given by Lord Rayleigh as determined by a photographic method. They have been redetermined by the authors by a direct *visual* observation of the track of a concentrated beam of sunlight in respective vapours contained in a cross tube, a nicol and double-image prism being used. The value of ρ for carbon bisulphide vapour is marked by Lord Rayleigh as doubtful, owing to the formation of cloud. The experimental value of ρ for the different liquids is given as determined by the authors at ordinary temperatures (35° C.). It will be seen in the case of benzene that there is a fairly good quantitative agreement between theory and observation. In the other cases the agreement is only qualitative, showing that the assumption of absolutely random orientation of the molecules in the

liquid and gaseous states and neglect of their mutual orienting influence is not fully justified. The fuller explanation of these discrepancies and of their changes at different temperatures is a matter for further investigation.

8. *Relation between Polarization of Scattered Light and Dispersion Formulæ.*

That the degree of optical anisotropy of the molecule may depend on the frequency of the incident light has been suggested by a number of writers, including the late Lord Rayleigh *, and as we have seen above, the examination of molecular scattering of light in liquids furnishes evidence that this is actually the case. Formulæ have been suggested connecting the degree of imperfection of the polarized light with the resonance frequencies of the molecules in different directions. Recently Havelock † has attempted, apparently with success, to pursue the matter further by utilizing the empirical dispersion formulæ for this purpose and has dealt with the case of hydrogen. It is obvious that the method may be extended further, and that the data made available by the observation of the authors on liquids with different wave-lengths enables a closer test to be made of the idea. We propose to deal with this more fully in a separate paper.

9. *Molecular Extinction of Light in Liquids.*

From the Einstein-Smoluchowski formula it follows that the intensity of a beam of light traversing a liquid would diminish owing to the scattering of light according to the formula

$$I = I_0 e^{-\alpha l},$$

where

$$\alpha = \frac{8\pi^3}{27} \frac{RT\beta(\mu^2 - 1)^2(\mu^2 + 2)^2}{N\lambda^4}.$$

This formula, however, requires correction for the effect of molecular anisotropy and will only be valid for those parts of the spectrum for which the liquid exercises no selective absorption, and it also assumes that the liquid contains no suspended matter. It has already been pointed out in a note in 'Nature,' that the corrected formula agrees with the experimental result obtained by Martin for dust-free benzene for wave-lengths 5461 and 4358 A.U. The determination of the extinction coefficient for other wave-lengths and for

* Born, *Verh. Deutsch. Phys. Gesel.* xvi. (1918) and see also *Zeit. für Physik*, xxxvii. (1921); and J. J. Thomson, *Phil. Mag.*, xl. (1920).

† *Proc. Roy. Soc.* May 1922.

other liquids (for which the coefficient is much larger than in water) should not present serious difficulties. Even with relatively short columns by the use of photo-electric cells balanced against one another, small extinction-coefficients should be capable of being determined with accuracy. Experimental work on this point is now in progress in the authors' laboratory.

10. *Absolute measurements and the Determination of the Avogadro Constant.*

Cabannes* has determined the Avogadro constant by means of absolute determination of the light-scattering in gases. Since the Einstein-Smoluchowski formula for the scattering of light in fluids contains the Avogadro number (the other quantities μ , T , R , β , and λ being known), the Avogadro constant may also be determined by observations on light-scattering in liquids. This has been done by the writers in the following way.

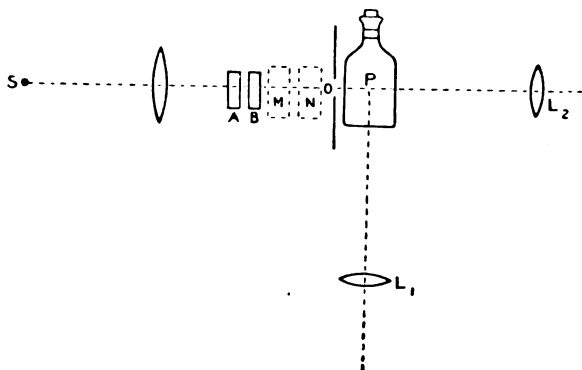
In order to be able to measure the amount of scattered light in terms of the incident light, it is necessary to use monochromatic light and also to cut down the incident light so as to enable comparisons to be made between it and the scattered light. As the source of light a mercury arc in silica was used. The 4358 line was used, all the other lines being filtered out by cuprammonium and quinine sulphate solutions. For reducing the incident light a solution of potassium dichromate was prepared. The arrangement was as shown in fig. 2.

The water that was used was distilled water that had been allowed to stand for a long time in a plane-sided glass bottle. The water was very clear, the motes all having settled down. The track when illuminated by a concentrated beam of sunlight was a fine blue one showing practically no motes. It was dead-black on all sides excepting apertures for ingress and egress of light, and observation of the track. The light from the arc S was focussed by a lens on the bottle through a rectangular aperture O. A and B were cells containing cuprammonium and quinine sulphate, respectively, to filter out the 4358 radiation. A square-sided bottle M contained the absorbing solution of potassium dichromate. The strength of the solution was varied by trial till the incident light was reduced in the proper ratio, such that its brightness was quite comparable with that of the track. To ensure that all the longer wave-lengths, 4916 etc.,

* *Ann. de Physique*, tome xv. (1920).

were absolutely cut off, another cell N containing a strong solution of cuprammonium was placed in the path of the incident beam. Wave-lengths smaller than 4358 had been initially cut off by the quinine sulphate solution, and the potassium dichromate solution reduces them further more equally well with the 4358 line. Thus it was ensured that both the reduced incident light and the scattered light were strictly of the same wave-length, a condition which is absolutely necessary since the intensity of the scattered light varies as λ^{-4} . The method of comparison consisted in photographing the track at P by means of a lens L_1 , at a definite distance r from the track, and in photographing the incident light at P by the same lens at L_2 and at the same distance r . When photographing the incident beam the

Fig. 2.



absorbing solutions M and N were placed in position to cut down the incident light. Photographs of both were taken on the same plate, the time of exposure being the same, and the final adjustments for the equality of the two tracks being made by altering the aperture of the lens L. The absorption of the solutions was determined accurately by means of a Nutting photometer, using a cell of a centimetre thickness to contain the solution. In calculating the total absorption, a correction for the reflexions at the glass surfaces of the cell and the bottle was made. The ratio thus obtained had to be further corrected owing to the fact that the incident light was slightly converging, while the diffused light is scattered in all directions. According to the Einstein-Smoluchowski formula, the total amount of light scattered in all directions is

$$\frac{8\pi^3}{27} \frac{RT\beta(\mu^2 - 1)^2(\mu^2 + 2)^2}{N\lambda^4}$$

per unit volume, which is distributed over a solid angle 4π . The fraction of the total diffused energy caught by lens L is only $a / \frac{16\pi r^2}{3}$ of the whole, where a is the area of the lens. In the case of the incident light the fraction of energy caught by the lens is $a/4\pi r^2 \sin^2 \frac{\theta}{2}$, where θ is the angle of convergence of light. Taking this correction into account the ratio was calculated. From this, and putting $R = 1.37 \times 10^{-16}$ per molecule; 42×10^{-12} dynes/cm.²; $T = 305^\circ$; $\mu = 1.337$, N was evaluated (taking into account the Cabannes factor) and found to be 7.3×10^{23} , which is of the right order of magnitude.

Summary.

The paper deals with the problem of molecular scattering and extinction of light in liquids, both from the experimental and the theoretical standpoints, and the following are the general results obtained:—

(1) It is shown that the intensity of the light diffused in liquids is not given by the Rayleigh law of scattering. The "Theory of Fluctuations" of density considered by Einstein and Smoluchowski, however, gives a quantitative explanation of the observed phenomena, provided account is taken of the influence of molecular anisotropy which, in general, is very important in the case of liquids.

(2) The light scattered transversely by liquids is, in general, very imperfectly polarized, in fact, far more so than in the case of the vapour of the same substance. It is shown that this fact receives explanation when we consider the general character of the distribution in the liquids of the molecules separately as regards *position* and *orientation*. The theory may be given a quantitative form, and enables the polarization in the liquid to be calculated when that of the vapour is known. Good agreement with facts is observed in the case of some liquids, but in others it is only qualitatively correct.

(3) In accordance with the indications of theory, the intensity of scattering increases with the temperature in liquids and becomes very large as the critical point is approached. The polarization of the scattered light tends at the same time to become more and more perfect.

(4) The state of polarization of the scattered light is found experimentally in liquids to be a function of the wavelength of the incident light, and this indicates that the observed optical anisotropy is probably connected with the

resonance frequencies of the molecules in different directions and with the dispersive properties of the substance.

(5) The absolute determination of the light scattering in liquids enables the Avogadro constant to be evaluated.

Further work with the subject is in progress.

Calcutta,
1st of June, 1922.

Note added in proof dated 11th Dec. 1922.—A fuller discussion of the effect of molecular anisotropy on the scattering and extinction of light in liquids, based on the electron theory of dispersion, will appear in a paper by Mr. K. R. Ramanathan shortly to be published. In his treatment, the fact that the electric polarization is not the same within the liquid as outside it is considered and taken into account.

LXIV. *Intelligence and Miscellaneous Articles.*

ON THE VISCOSITY OF GASES IN A TRANSVERSE ELECTRIC FIELD.

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN a paper published in your June number of 1922 on "Viscosity of Air in a Transverse Electric Field," Mr. Satyendra Ray communicates experiments to test whether there is a change in the viscosity of air in a transverse electric field. In *Zeitschrift f. Physik*, I am publishing now a paper which treats this subject from the point of view of the kinetic theory of gases, assuming that the molecules are electric quadruples acquiring in an electric field a momentum proportional to the field-strength. In a field of 100 C.G.S. units the ratio of the viscosity in a transverse field to the viscosity without field would be

$$\text{for nitrogen} = 1 - 4 \cdot 10^{-9},$$

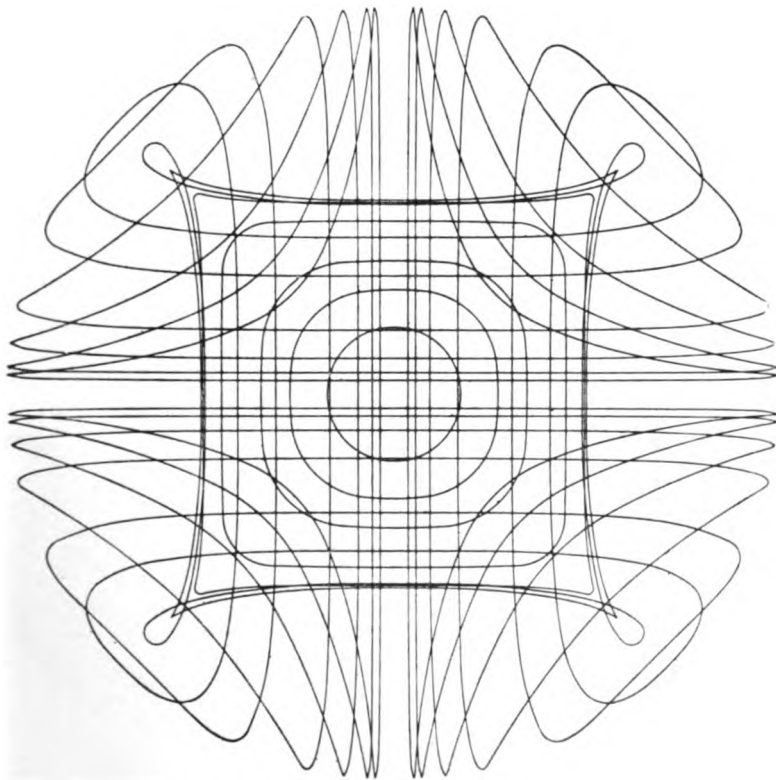
$$\text{for oxygen} = 1 - 3 \cdot 10^{-9}.$$

Mr. Ray found the absence of change in the viscosity of air greater than or equal to 0.3 per cent. in a transverse field of in 60 C.G.S. units, which is in accord with my calculations.

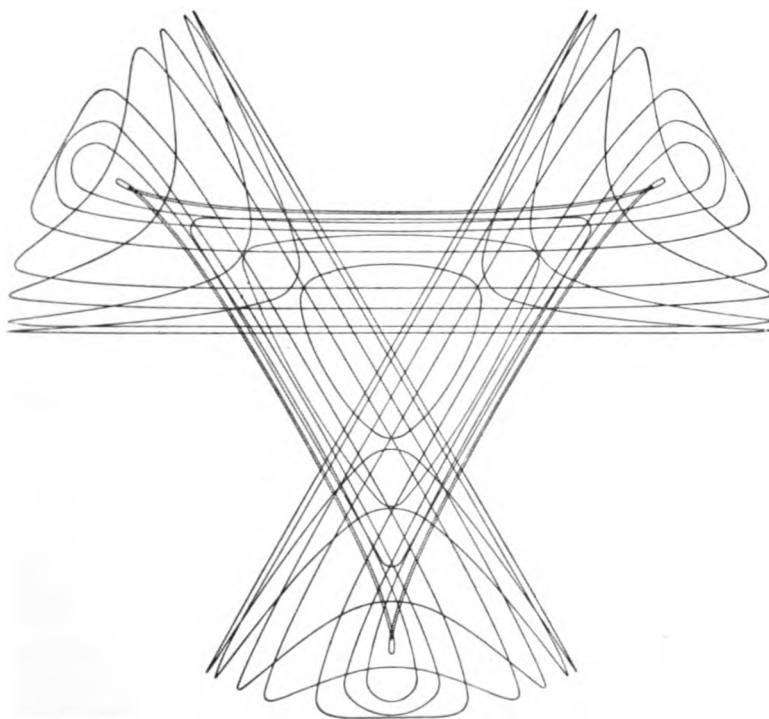
Institut f. theoretische Physik
an der Universität, Vienna.
Dec. 7, 1922.

Yours faithfully,
H. SIKK.

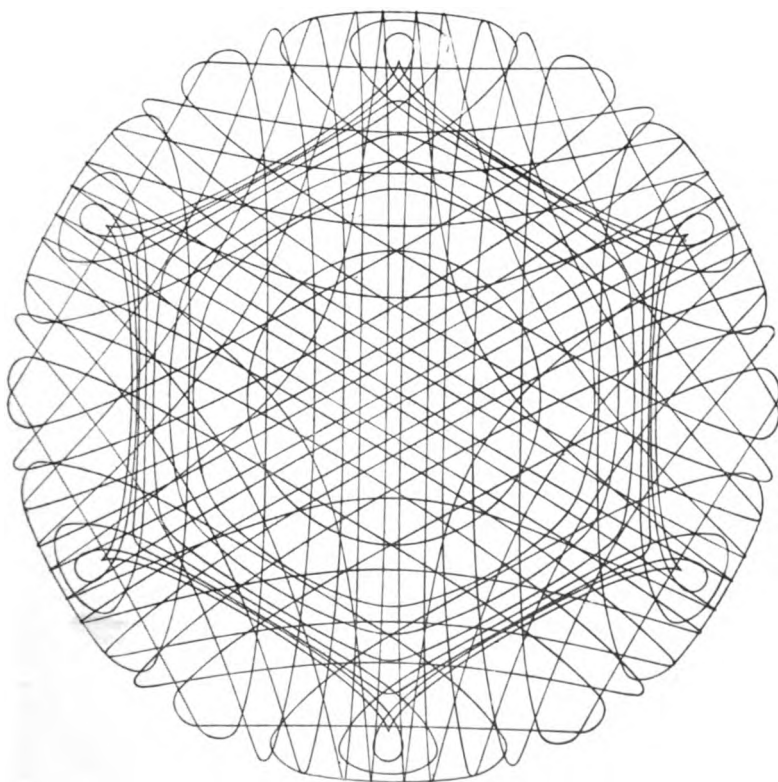
FOUR-FOLD GYROSCOPIC CURVES.



THREE-FOLD ALGEBRAICAL GYROSCOPIC CURVES.



ALGEBRAICAL GYROSCOPIC CURVES
in six branches.



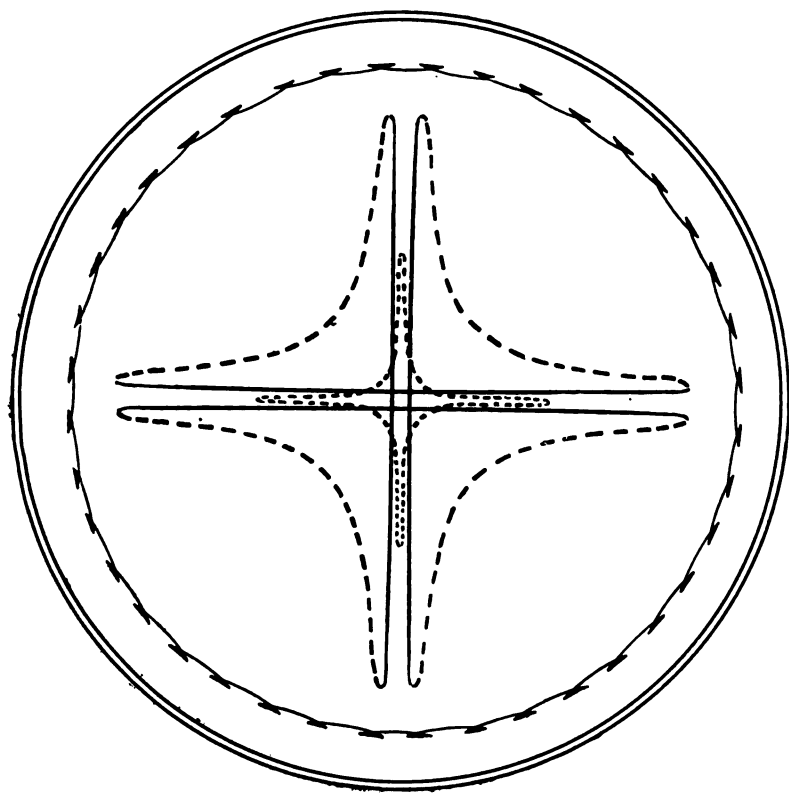
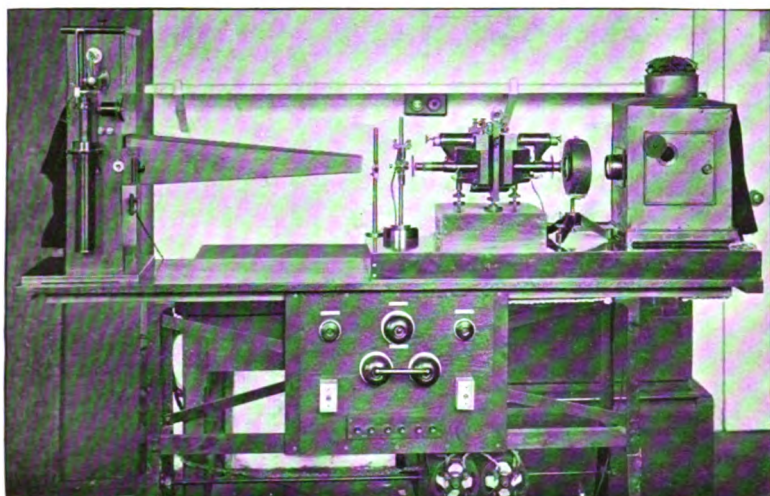
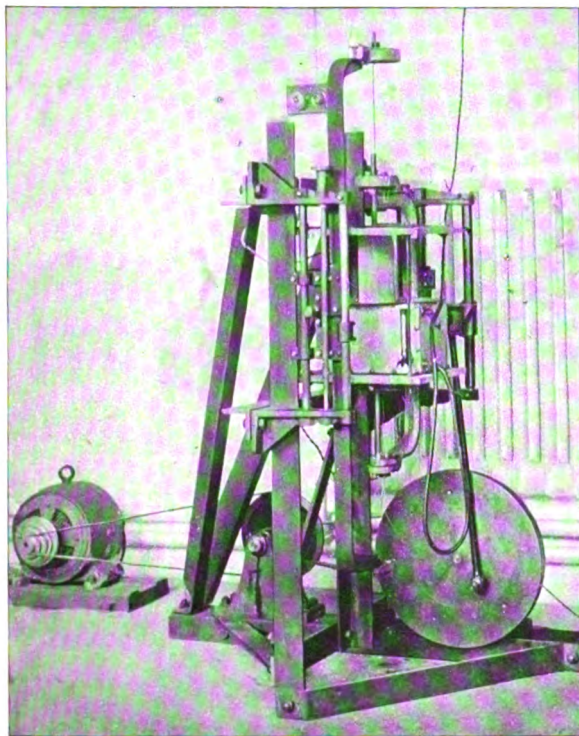


FIG. 1.



Photograph of Einthoven Galvanometer.

FIG. 3.



Photograph of Apparatus.

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

APRIL 1923.

LXV. *The Reaction consequent upon the Evaporation of a Liquid and upon the Emission of Vapours from Small Orifices.*—PART I. *Argument.* PART II. *Appendix.*
By Prof. W. G. DUFFIELD, D.Sc., University College, Reading*.

INTRODUCTION.

THE object of this communication is to draw attention to a type of interference between the molecules of a vapour and those of an external medium, which appears to play a considerable part in the phenomenon of evaporation and in the discharge of a vapour from a boiler.

It deals also with the manner in which a vapour is discharged into the atmosphere from a boiling liquid and with the reaction consequent upon the discharge of molecules from a boiler maintained at a steady temperature and pressure, and with certain phenomena associated with saturated vapours which have to be considered in the light of the existence of molecular interference.

The paper is divided into two parts:—the first sketches the main features of the investigation and describes the results; this we have termed the *Argument*; the second, which consists of an *Appendix* divided into several Sections, comprises fuller details of the experiments described in the first part, together with a certain amount of mathematical treatment, whose inclusion in the outline of the dissertation would tend to obscure the trend of the discussion.

* Communicated by the Author.

Phil. Mag. S. 6. Vol. 45. No. 268. April 1923. 2 T

PART I.

THE ARGUMENT.

The Origin of the Investigation.

IN the course of a series of experiments upon an electric arc burning in air, it was discovered that each pole behaved as though there were a mechanical pressure upon it which caused it to move away from the opposite pole*. It is not necessary here to discuss this phenomenon, it is sufficient to state that various explanations of this pressure suggested themselves, amongst others that it was the reaction consequent upon the evaporation of carbon atoms from the hot poles. It was the necessity for testing this experimentally which led to the present investigation; the results of some of the earlier experiments have been briefly stated in the papers to which reference has been made. A somewhat similar problem had previously confronted Osborne Reynolds, who gave reasons, stated in Section 10 (Appendix), for expecting a reaction upon an evaporating surface.

Evidence of Interference in the Process of Evaporation.

The investigation has been carried much further than the original problem demanded, which was merely to discover whether in the process of evaporation or boiling into the open air, there were any measurable mechanical reaction upon the surface from which the molecules were issuing. This was, however, the first matter submitted to experimental test. Water and ether were the substances found most suitable and, briefly, it may be stated that no measurable reaction was observed when these evaporated into the open air. This experimental fact led to an examination of the reasons why it is absent, or at least too small to be measured.

There is a real and, I believe, a new problem here: for suppose that there is an escape of molecules of water vapour at the rate of something like .03 gm. per second (as in an actual experiment), and that the molecules of steam are escaping from the liquid with a speed which is of the order of magnitude associated with a gas molecule at the temperature of the experiment (roughly 7×10^4 cm. per second for steam at 100°C.). This is, I believe, the generally, but not universally, accepted view; it was adopted by O. Reynolds (*loc. cit.*), and experiments by Knudsen seem to support it.

* Duffield, Burnham, and Davis, Phil. Trans. Roy. Soc. A. 220, p. 109 (1919). Proc. Roy. Soc. A. 97, p. 326 (1920).

The matter is further considered in Section 4, Appendix, but we adopt it here provisionally as a working hypothesis. On this basis we see that the surface should be losing momentum at the rate of $\cdot 03 \times 7 \times 10^4 = 2100$ dynes, which is nearly equal to the weight of 2.14 gms. This is, therefore, the order of magnitude of the force to be expected if the molecular projections were the only factor to be taken into account; if only the fastest molecules were projected the rate of loss of momentum would be still greater; on the other hand, if the projection were at random instead of normal to the surface, we should divide by $\sqrt{3}$.

In another experiment, the evaporation proceeded so rapidly that the rate at which the liquid lost momentum, on account of the projection of molecules, corresponded to the weight of 11.4 gms. Obviously no very refined experiment should be required to detect so large a reaction, and that is why we have been content in the first instance with a rough experimental investigation whose object was to detect whether or not there is a reaction of this order of magnitude.

The first experiment was conducted by allowing ether to evaporate from the pan of a balance and observing the rate at which the pointer moved (Section 1)*. Subsequently (Section 2), it was shown that it was legitimate to experiment with a liquid which was boiling, because it was found that a boiling liquid does not in the main, or even largely, discharge its vapour through the bursting of bubbles, but by the passage of the material through the bubble-wall after the bubble has risen to the surface; so that in its final stage the phenomenon of boiling is closely allied to that of evaporation in that the essential action takes place at the surface.

A second set of experiments was therefore carried out in which a liquid was boiled upon the pan of a balance (Section 3). The writer would be the last to claim that these experiments are of a refined character, but they certainly appear to be adequate to determine whether the molecular projection was the only factor involved in the process of evaporation and boiling into the open air.

In none of the experiments was any pressure upon the surface observed, and we are well within the limits of experimental errors when we say that we could easily have detected a reaction equal to the hundredth part of that whose existence we wished to test.

* The reference is to Section 1 of the Appendix forming Part II. of this paper. Subsequent references will be similarly abbreviated.

The problem is to account for the absence of any measurable reaction.

Is it absent because (1) the general view is wrong that the molecules issue with the velocity we have assigned to them; do they, instead of being projected like bullets, just drop off? Do they suffer so much in velocity in penetrating the surface layer? Do they, in fact, behave like electrons liberated photoelectrically from a metal at the threshold frequency? We devote Section 4, Appendix, to a consideration of this point, and as the evidence obtained *in vacuo* points to a high velocity of projection, it seems that this is not the explanation, so we proceed to consider the other alternative (2), namely, that there is some compensating interaction between the projected molecules and the molecules of air or previously evaporated material in the space above the liquid, which prevents the loss of momentum of the projected material from becoming evident as a pressure upon the surface?

The gist of the experimental evidence, though not absolutely conclusive, is that the evaporative reaction *in vacuo* is powerful and in air imperceptible, hence we conclude that the explanation lies in this latter alternative, and what we must next proceed to do is to examine the effect upon the motions of the molecules of air or vapour above the liquid of the projection among them of a large number of molecules moving with high speeds from the liquid below. We must observe two precautions in dealing with the problem—it would be misleading and erroneous to treat the problem as though the evaporated material were introduced into the atmosphere as an ordinary mass of gas with the usual Maxwellian velocity distribution; this is not the case, since the molecular motions are all in the forward direction though precisely how distributed about the normal to the surface is not at present known. Moreover, the permanently escaping material is not to be treated as saturated vapour; this we may see by comparing the number of molecules which would cross unit plane within a saturated vapour with the number actually lost by the same area of a liquid surface under vigorous boiling. As we show later, the ratio is not likely to be much less than 5000 to 1. Or we may put the matter thus:—The quantity of vapour crossing unit plane in a saturated vapour in a second at atmospheric pressure is obtained by writing $\Pi = 10^6 = 2mnv$, where n is the number of molecules crossing unit plane in one second with velocity v normal to it, whence for steam at 100° C. the mass $mn = 10^6/2v = 10^6/2 \times 6.6 \times 10^4 = 7.6$ gms.

This is enormously greater than the greatest rate of boiling attained, namely .0015 gm. per sec. per unit area.

It is true of course that the newly evaporated molecules will, after projection, find themselves amongst previously evaporated material, and that the whole space may be saturated, but the point is that the material as it issues is far from possessing the density of saturated vapour; we might indeed imagine so slow a supply of heat that only one molecule issued from each sq. cm. in a second. It should be clear from this that the ordinary equations relating to the mass-motion of a vapour are not applicable to this problem; we proceed therefore from another point of view.

If the external molecules which are set in motion by collision with the projected material were originally stagnant, at rest, the momentum of the whole mass would still be that of the projected material. Imagine a platform on which a thousand cannon were mounted, all pointing in the same horizontal direction, and each of which fired a cannon-ball per second. The reaction upon the platform would be the same, whether the space before it were empty or were occupied by a large number of similar balls suspended by cords which broke when the balls were struck. The loss of momentum per second by the platform would be the same, but there would be a different number of balls in motion in the two cases—in the first a thousand would be set in very rapid motion in each second, whereas in the latter there would be many thousand moving with much smaller speeds, but representing the same total momentum away from the platform. The full recoil would be felt by the platform in each case.

Clearly, since in our actual experiments an evaporating surface remains sensibly at atmospheric pressure even when discharging molecules with enormous velocities, there must be a further factor to be taken into account.

It was suggested that the condensation of the vapour into water above the liquid might occasion a reduction in the pressure which would just balance matters. This was tested, not by the rather insensitive balance method, but by using a jet of steam and observing the reaction upon the vessel from which it was issuing by a delicate torsion method, both when the steam was condensed upon a cold body placed close to the orifice, and also when a body at a temperature over 100° C. was substituted. Though in one case the condensation was vigorous and in the other was absent, no difference in the reaction was observed. The areas of the hot and cold bodies were 100,000 times that of the orifice, and they were

placed in turn at distances varying from 7 cms. to 0.2 cm. from the orifice. This is strong evidence that condensation, as usually understood, is not the cause of the phenomenon.

What then is the further factor to be taken into account? In the writer's opinion it is that the molecules of the external medium are in motion and that this is profoundly affected by the projected material.

The liquid is being continually bombarded by molecules of air or vapour whose impacts occasion the usual gas pressure, but, as the rate of evaporation increases, some or all of these suffer encounters with the molecules projected from the liquid, so that they are prevented from communicating their full momentum to the surface.

This may happen either through the deflexion of the molecule or the reduction of its velocity normal to the surface as the result of a collision or series of collisions. The precise mechanism whereby the momentum is diverted or neutralized we do not propose to examine here; we should not, however, dismiss lightly the possibility of some collisions being of an inelastic character, because Wood has shown from spectroscopic evidence that a newly evaporated molecule of mercury may, instead of condensing, attach itself to a molecule of hydrogen in the space above the boiling liquid, and there is also in a vapour always the possibility of molecular association. Also we find Langmuir urging the inelastic nature of the encounters close to an evaporating solid surface.

Our view thus is that there is a type of interference between the rising molecules and those directed downwards from above, and the reason why the pressure upon the surface is not the simple sum of the atmospheric pressure and that due to the recoil is that the downward stream fails to impart to the surface the momentum which has been deflected or otherwise absorbed.

It is as though our gun-platform were being bombarded by enemy fire, which we can picture as occasioning a pressure which might be measured by the compression of a spring. Upon our opening fire, there is an additional reaction if our cannon balls do not strike those of the enemy (*i. e.* if the cannon ball density is low), but if they do collide in such a way that each ball stops or diverts an enemy ball, the reading of the spring will remain unaffected by the discharge of our guns, since each discharge both contributes a certain amount of kick to the platform and robs it of the impact of an enemy shell.

But it is not infinitely probable that each enemy shell will

meet one of ours in such a way as to be prevented from delivering its momentum to the platform, so the neutralization is not likely to be complete unless the discharge rate is very great. The amount of momentum stopped depends, for example, upon the size of the shot and the number fired in each second. This then is much what is happening in the case of a liquid which is evaporating or boiling—it depends upon the rate of evaporation how much of the external atmosphere is prevented from exerting its pressure upon the surface.

In the experiments we have described the number of molecules escaping per second was always a very small fraction of those incident upon the surface in that time:—for example, for a moderately rapid rate of boiling, 0·0015 gm., or 5×10^{19} molecules, escaped per second from each sq. cm., whereas the number incident from above was approximately $3 \cdot 4 \times 10^{23}$ in the same time, so that the number escaping was less than the 1/5000th part of those with velocities directed towards the surface. In no case was this rate of evaporation greatly exceeded, so to test our theory it becomes increasingly important to find other means whereby we may achieve a greater ratio between those emitted and those approaching the surface from without.

Before discussing these, there is one simple case of some theoretical interest—suppose that even with small discharges *all* emitted molecules were to meet external molecules in effective encounters; let us gradually increase the rate of discharge; we should expect to find no reaction upon the liquid so long as there were molecules in the external medium with velocities directed towards the surface, which could be stopped or diverted by those emitted. When the latter are all met compensation ceases, and any additional molecule projected from the liquid will then contribute a reaction which cannot be balanced by any interaction with the atmospheric molecules, so a pressure in excess of that of the atmosphere will be experienced. It is easy to see, or if there is any difficulty, Section 8, which will be referred to later in the Argument, will make it clear, that the limiting rate of discharge without reaction occurs when twice as many molecules leave the surface as would have struck it from above if there had been no evaporation; a simple calculation (*loc. cit.*) indicates that if the liquid and the vapour above are both sensibly at 100° C., the limiting rate is approximately 15 gms. per second per sq. cm., so, for the particular case we have imagined, we should expect zero reaction below this rate and a rapidly increasing reaction

above it. We shall see later that there is some indirect experimental evidence in accord with the figure we have obtained.

We may now return to our search for a method of testing the interference between the emitted and external molecules. Two means suggested themselves—we may either alter the number of external molecules or we may increase the number emitted.

The former was tried first:—the theory indicated that if the external atmosphere were removed, we should obtain the full effect of the reaction due to the projection of molecules and, consequently, that we should find a measurable reaction. The experiment has already been described in Appendix, Sections 4 and 5, and as a powerful reaction was observed, it was in accord with our theory.

As this mode of attacking the problem did not lend itself readily to quantitative measurement, it seemed desirable to find a means of increasing the rate of discharge per sq. cm. of high speed molecules into the atmosphere at ordinary pressures. It occurred to the writer that the efflux of steam from a small aperture in the side of the boiler might be made to fulfil the necessary conditions. By using a large boiling surface and a small aperture the number of molecules driven out in each second per unit area may be increased enormously.

Evidence of Interference in the Discharge of Vapour from an Orifice.

If heat were supplied to a boiler at such a rate that the wall and contents always remained at a uniform temperature, it is clear that the molecules would issue into a vacuous space with velocities appropriate to the temperature. It seemed, therefore, legitimate to regard the effect of discharging into an external atmosphere as compounded of an effect due to the issue of these molecules with their temperature velocities and that due to the external medium after collision with them. It seemed very probable that across some section, not necessarily identical with the plane of the aperture and not necessarily within the boiler, it would be permissible to treat the discharge as we have already treated that from a liquid surface. Indeed, it seems reasonable to imagine that across this section, which we may designate as the "effective aperture," provided the boiler is maintained at a steady temperature and pressure, the molecules escape with the same speed as that with which

they enter the vapour space from the liquid. This point is argued in Section 6, Appendix. It marks a departure from the usually accepted idea of the efflux of vapour from an orifice, but for the case considered, namely that in which the efflux is due to the evaporation of a liquid, it is believed to be correct. It is possible that the reason why it has not been recognized is that the interference between the emitted molecules and those outside the vessel has masked the effect.

The case differs, of course, from the escape of a gas or vapour into the atmosphere from a vessel at a higher pressure, because the pressure will not then be steady, and steadiness of temperature and pressure are essential conditions, but we can attain steady conditions if we introduce molecules to the same number and with the same speeds as those which depart. This is automatically done in the case of the boiler with a hole in it, if we keep the supply of heat steady.

It is almost as though we could regard each molecule introduced into the vapour space as a little piston moving with the molecular velocity whose effect would be to drive one molecule out from the "effective aperture" with the same speed.

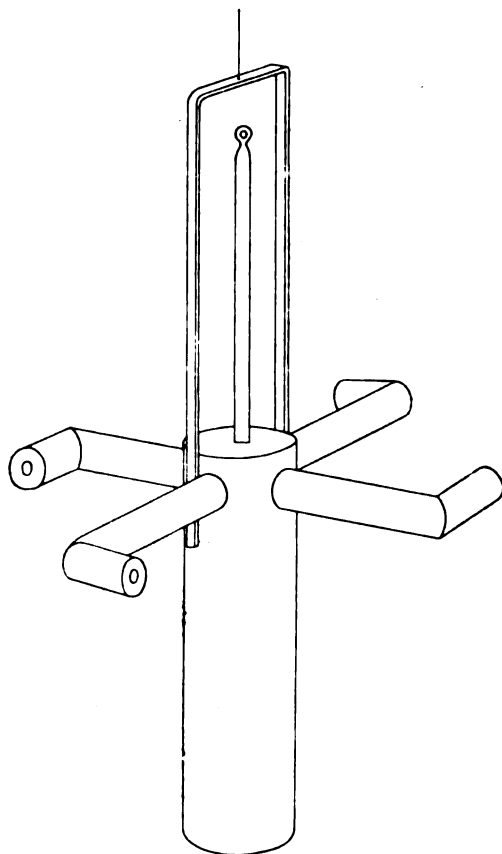
We may repeat what we have already said concerning the material evaporated from a liquid, namely that the escaping vapour cannot be treated as a mass of saturated vapour with the density ordinarily associated with that temperature.

The justification of this and the preceding theory of molecular interference lies in its simplicity and its ability to give a reasonable explanation of experimental results, as we shall now attempt to show. We shall first outline the experimental results, then derive a mathematical formula from the theoretical considerations which we have already adduced, and finally indicate the measure of agreement between them.

The experiments were carried out with a form of Hero's engine, consisting of a boiler (fig. 1) suspended by a torsion fibre, and so disposed that the issue of steam twisted this through an angle which could be measured. The total reaction, R , in excess of the atmosphere, was thus calculable. The apertures at the ends of the arms were circular holes in thin brass sheet; their size and number could be varied. Further details of the apparatus and method of experimenting are relegated to Section 7, it is sufficient for the purpose of the Argument to indicate the relationship between R and D , the quantity of steam discharged per second, for apertures of different diameters.

When the aperture was as large as the undisturbed surface of the boiling liquid, it was not possible to obtain a rate of discharge which would occasion any measurable recoil—this appears to be strong evidence of the existence of interference between the issuing and external material: in one

Fig. 1.



experiment the rate at which the boiler lost momentum on account of the projection of molecules would have occasioned a twist of 30,000 degrees if there had been no compensating interaction with the surrounding medium, or if it had been discharging into a vacuous space, but no twist was observed.

Other experiments with less sensitive suspensions are quoted in Table I. to the same effect.

TABLE I.

The Reaction observed with large apertures.

Observers : W. G. Duffield & J. S. Burgess.

Ratio of area of apertures to boiling surface area.	Mass evaporated per second. D gms.	Deflexion observed.	Deflexion which would have been observed if there had been no interference.
1	0.016	-5°0	6300°
	0.077	0°	32000°
	0.026	0°	9510°
	0.086	+4°0	30200°
.75	0.044	0°	16300°
	0.018	0°	810°
	0.034	+1°8	12300°
.5	0.024	2°0	1060°
	0.040	2°0	1770°
	0.057	2°2	20700°
.25	0.032	1°6	11600°
	0.007	4°0	2580°

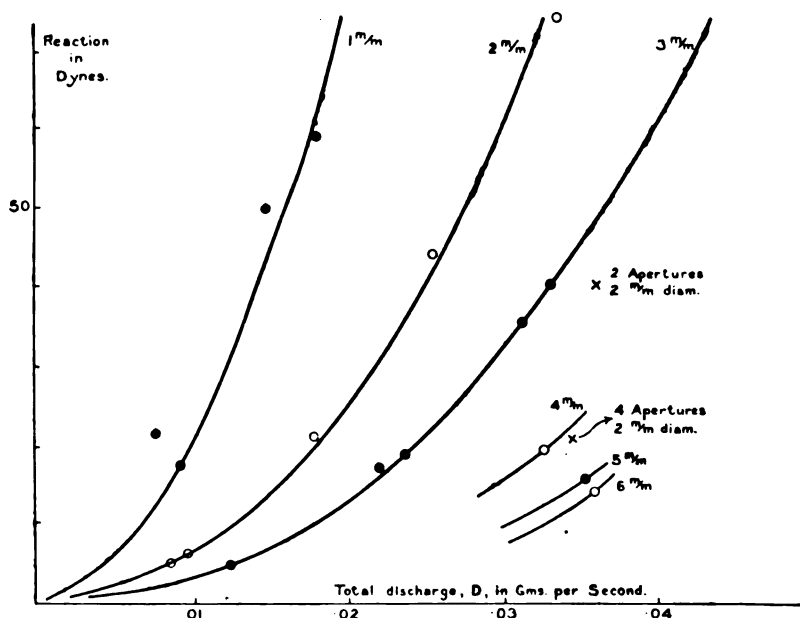
Torsion wires of varying sensitivities were used in different experiments.

Upon diminishing the aperture area a small reaction was observed which increased slightly as the aperture was further reduced in size; this is shown by the latter half of Table I., but the reaction is still almost negligibly small in comparison with the effect which would have been produced if the atmosphere had been stagnant.

Further Experiments upon the Discharge of Vapour from Small Orifices.

The results of experiments with still smaller apertures are given in Table III., Section 7, from which it will be seen that reactions of the order of some hundreds of dynes were obtained; it is sufficient here to indicate the results graphically, as in fig. 2, where D and R are plotted. The interesting fact emerges that for a given discharge rate the reaction is

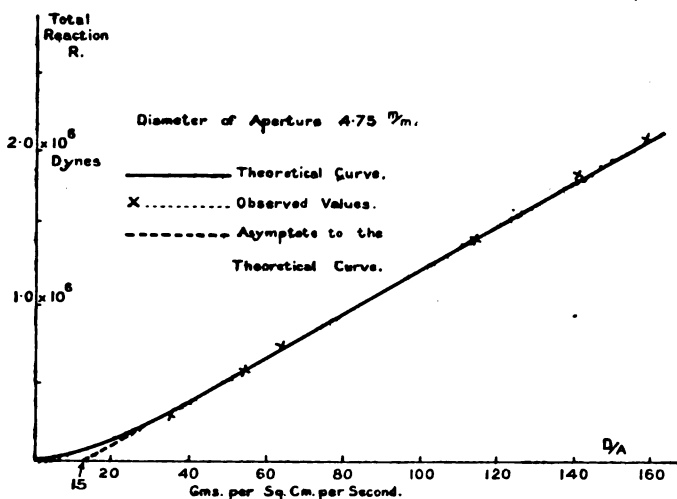
Fig. 2.



greatest when the aperture is smallest. The effect of doubling the number of apertures is approximately to halve the reaction. We note the rate at which the reaction varies with the discharge; at first it is approximately parabolic but subsequently becomes more nearly linear. The character of the graph for very high rates is best shown by fig. 3, which represents the results of a series of observations by Rosenhain with an orifice 4.75 mm. in diam. (*vide* Section 7); here, however, we have plotted the reaction, R , against D/A ,

the discharge per unit area per second, instead of D , as in the previous figure. Disregarding the theoretical curve, which will be discussed later, we note that the graph shows a nearly linear relationship as high values of D/A are reached.

Fig. 3.



Theoretical Investigation of the Discharge from Orifices upon the Interference Hypothesis.

Let us now see if our theory can account for the shapes of these curves. In dealing with this problem, which is really a statistical phenomenon of considerable complexity, we shall make certain assumptions which will greatly simplify the mathematical treatment; they should at least provide us with the *form* of equation relating the reaction to the discharge. For example, we suppose all molecules to possess the average velocity associated with their temperature on the kinetic theory, and we also suppose that interference between two streams of molecules, instead of reducing the velocities of a large number of them, completely stops a certain fraction of each stream, the remainder proceeding with undiminished velocities; these simplifications would probably affect the values of the constants in our final

equation if we were to attempt to evaluate them from probability considerations, but, as we shall determine their value from the data of a particular experiment, it is probable that our results do not suffer.

Our view of the phenomenon of the discharge is as follows :—

From the “effective aperture” a certain number of vapour molecules n_1 are discharged in each second, a certain number enter in each second, and L is the excess of those emitted over those which enter in that time. These n_1 molecules leave with an average velocity appropriate to the temperature, as already explained (Section 6), of which v_1 is the average component normal to the orifice. Their distribution about the normal to the orifice is unknown, it may be that it is a Maxwellian distribution in the forward direction only, or the projection except very close to the edges may be normal.

There will be a reaction upon the vessel due to these, amounting to mn_1v_1 .

The other source of pressure upon the vessel arises from its bombardment by molecules from the atmosphere, which we may assume to be molecules of water-vapour. These, if there were no molecular interference, would contribute a pressure to each unit area of the effective aperture equal to the rate at which they deliver momentum to it, but the fact that collisions will occur between these molecules and the projected molecules occasions a reduction in the momentum which reaches it from the external medium. An important part of our problem is to find out how much of this atmospheric momentum is prevented from reaching the vessel, and how much gets through to it; we shall, for the present, denote by β the fraction which is prevented from reaching unit area of the effective aperture. We shall see later that it is likely to be a simple function of the rate of discharge of vapour from the vessel. The conditions near an evaporating surface and near an orifice are set forth in Sections 8 and 9. The problems are regarded as identical, except that the question of reflexion does not arise in the case of the orifice, and that simplifies matters. The orifice problem is free also from the possibility, which arises when using a horizontal discharging surface, of some condensed vapour falling back upon the liquid. We may note that if this did occur in the evaporation experiments, which the

writer doubts, it would mean that there was more interference than was supposed, because the original discharge would have been underestimated.

In the case of the discharge from an orifice the formula (see Section 8, Equation 11) for the total reaction R upon a vessel from which steam is issuing at the rate of D gms. per second from an aperture of area A is given by

$$R = Dv_l + \frac{\Pi A}{2}(r-1) - \Pi A \frac{r+1}{2}\beta,$$

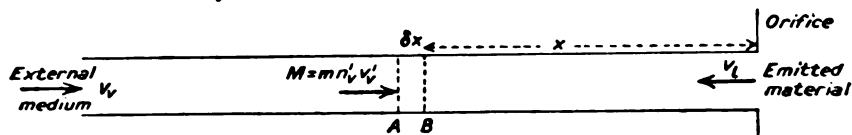
where r is the ratio of the average velocity v_l of the discharge in the normal direction, to v_v , the velocity with which an external molecule strikes the surface. The assumption has been made that interference operates by reducing the number of external molecules which penetrate to the aperture rather than by reducing their velocity.

If we wish to compare this theoretical result with those obtained experimentally, we require further information regarding the value of β .

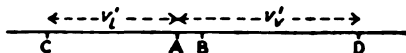
The simplest way of examining the nature of the function β is to look upon the ejected material as "absorbing" the momentum of those molecules of the external medium which would have entered the vessel if there had been no discharge. We do not know precisely how the "absorption" takes place, whether the external molecules are merely diverted from the orifice, or whether their momentum is partially neutralized by non-elastic collision with the issuing molecules. We may obtain the *form* of the equation relating the loss of momentum to the rate of discharge of the material by considering a simple case:—

Assume that the jet is parallel and that condensation does not occur in the range under discussion; assume also that all the issuing molecules move in a direction normal to the aperture, and that the pressure of the external atmosphere is due to a stream of molecules directed along the axis of the jet, each molecule being assumed to possess the average velocity of the stream. There are thus two opposing streams of which the former tends to neutralize or absorb the momentum of the latter. Let the jet be of unit cross-section, and let M be the total momentum of all the particles of the external medium which penetrate to a distance x from the orifice in each second. In traversing a further distance δx , there will be a further loss or absorption of momentum, δm , in each second. We should expect this to be proportional

to M and to the number of emitted molecules in the volume δx . We may examine the matter as follows:—



Let n'_e be the number of molecules of the external medium which cross the section A, distant x from the orifice, in each second. Let their average velocity at this point be v'_e . We require in the first instance to know the total number of collisions made by these n'_e molecules in traversing δx . We shall first find the probable number of encounters with the emitted molecules which a plane area at A would suffer if it were moved forward to B:—The molecules of



emitted material which are at A at the beginning of a particular second would, if their velocity were maintained, be at C at the end of that interval, where $AC = v'_i$, the velocity of that material at the point x . In the meantime the plane would have moved from A to D, a distance v'_e , and so would have encountered all the molecules contained in the length CD in one second, where $CD = v'_i + v'_e$. But the time taken by the plane to go from A to B is $\delta x / v'_e$, consequently, in going this distance the plane sweeps through a column of molecules whose length is $(v'_i + v'_e) \delta x / v'_e$.

Let there be N_x projected molecules in each unit length near the point x at any instant, then the number of molecules encountered by the unit plane is

$$N_x (v'_i + v'_e) \delta x / v'_e.$$

But the effective area of the n'_e molecules which cross plane A in one second is $\pi \sigma^2 n'_e$, where σ is the molecular diameter, so the probable number of collisions between the two streams in the region δx in one second is

$$\gamma \pi \sigma^2 n'_e N_x (v'_i + v'_e) \delta x / v'_e,$$

where γ is a constant. Of these a certain fraction λ may be classed as effective in absorbing the momentum of the external medium.

λ is possibly a function of the relative velocities of the molecules in the two streams, but there are two reasons for

regarding it as approximately a constant, (1) because Jeans found that the expectation of the velocity of an individual molecule after an elastic encounter being in the original direction varied only from .33 to .5, though the relative velocities varied from 0 to ∞ , and (2) because the case which we shall follow most closely is that in which the absorption of momentum is due to a diminution in the number of molecules reaching the surface, the velocities of the remainder being unaffected, though a similar expression results from a consideration of a general reduction in the molecular velocities. On this basis we see that each effective collision deprives the oncoming stream of mv_v' units of momentum; consequently the amount of momentum absorbed is given by

$$\delta M = \lambda \gamma \pi \sigma^2 m n_v' v_v' (v_l' + v_v') N_x \delta x / v_v,$$

which, since $M = m n_v' v_v'$, and $v_l' = v_l$ and $v_v' = v_v$, becomes

$$\delta M = \lambda' M N_x \delta x (v_l + v_v) / v_v,$$

where λ' is another constant. Writing $v_l/v_v = r$, as before, we have

$$\delta M/M = \lambda' (r+1) N_x \delta x.$$

We may integrate this from the region $x = v_l$, where we should have $M = m n_v v_v$ to the aperture where $x = 0$, and M has the value M_0 , thus:—

$$\int_{M=M_0}^{M=m n_v v_v} \frac{dM}{M} = \lambda' (r+1) \int_{x=0}^{x=v_l} N_x dx.$$

The quantity under the integral on the right-hand side is the total number of molecules, n_l , emitted in one second, whence

$$\begin{aligned} \log M_0 - \log m n_v v_v &= -\lambda' (r+1) n_l \\ &= -\frac{\lambda'}{m} (r+1) m n_l = -\mu (r+1) m n_l, \end{aligned}$$

where μ is a constant for a given set of external conditions, hence

$$M_0 = m n_v v_v e^{-\mu(r+1) m n_l}.$$

If, instead of assuming that all the material were confined to a parallel jet normal to the aperture, we regarded it as distributed over a hemisphere, we should expect to obtain an expression of the same form but with a constant of different value.

We have previously written β for the fraction of the momentum $mn_r v_r$ which was directed towards, but failed to reach the effective aperture (Section 8, Appendix), consequently

$$\beta = 1 - e^{-\mu(r+1)mn_l}. \quad \dots \quad (13a)$$

Let us now apply this formula to the jet experiments. For reasons given in the note below, we write $mn_l = mL = D/A$, where, as before, D is the discharge from area A , whence

$$\beta = 1 - e^{-\mu(r+1)D/A}.$$

Substituting in equation (11), Section 8, Appendix, we have

$$R = Dv_l - \Pi A + \Pi A \frac{(r+1)}{2} e^{-\mu(r+1)D/A}. \quad \dots \quad (14)$$

Note.—We have written L the excess number of molecules emitted over those which return, in place of n_l , the total number emitted; this was originally an assumption but it seems amply justified by results and is probably correct for two reasons: first, because, as we have stated in Section 6, it is doubtful in the jet experiments if any of the $n_r(1-\beta)$ molecules actually reach the vessel, in which case the observed loss, D , is the loss of all the n_l molecules, and secondly, because in the present case we deal with what may be called “external” interference only, *i. e.* interference *additional* to that which may take place when the exchanges are equal and there is no loss of weight; the latter type of interference we may term “internal,” and, as we shall see, there is some evidence that it is of importance in the process of evaporation of a liquid into its own vapour. Thus only the excess, L , will be involved in the shielding action.

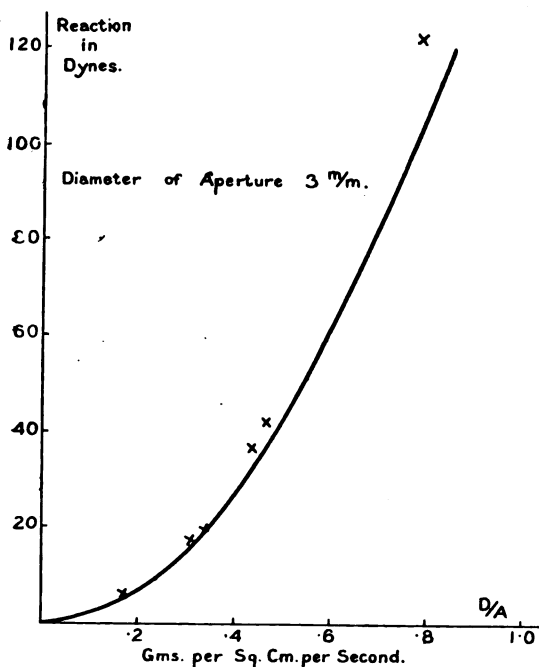
In order to be consistent we have taken $mn_r v_r$ as equal to $\Pi/2$, ignoring the possibility of a diminution of this quantity of momentum as it penetrates the stream of projected molecules—strictly speaking n_r is not the total number of molecules which would have crossed the aperture if there were no projection of molecules from it, but the number which would have crossed it if there were equality of exchanges, *i. e.* if $L=0$. This aspect of the subject is further discussed in Section 10, Appendix, and on p. 665.

We may note that if L could not be regarded as equal to n_l in the jet experiments, μ would vary slightly with the discharge rate and the value we obtain for it would be its limiting value when $L=0$. Our treatment of Internal Interference on p. 665 would not be affected.

Application of Formulæ to Experimental Results.

Let us now see if the equation (14) which we have obtained is in accord with our experimental results. Unfortunately the constant μ is not obtainable from theoretical considerations, while we remain in ignorance of the precise mechanism whereby a collision is rendered effective; we require to know wherein an effective differs from an ineffective collision. We may, however, evaluate μ from a single series of observations and test its applicability to other series. If our equation be tested this way we have very excellent evidence that it is of the right form.

Fig. 4.



From the series of observations with the .53 mm. aperture it was found that μ was a constant and equal to 0.033. Introducing this value into the equation and solving for values of A appropriate to the different apertures, we find the reactions plotted in figs. 4, 5, 6, and 7, full lines, for different values of D/A . It will be seen that in all cases the observed reactions fall very approximately upon the theoretical curves, showing a very satisfactory measure of agreement

Fig. 5.

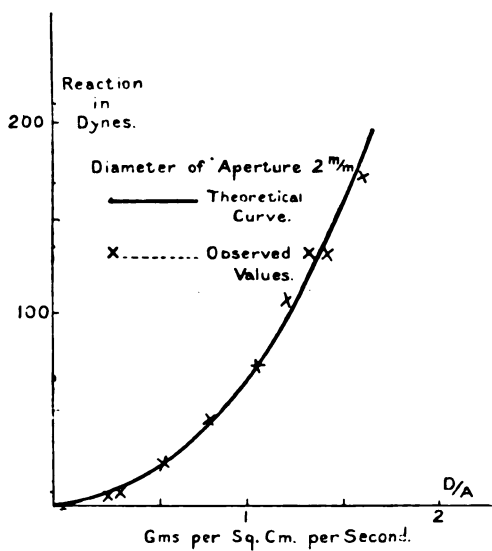
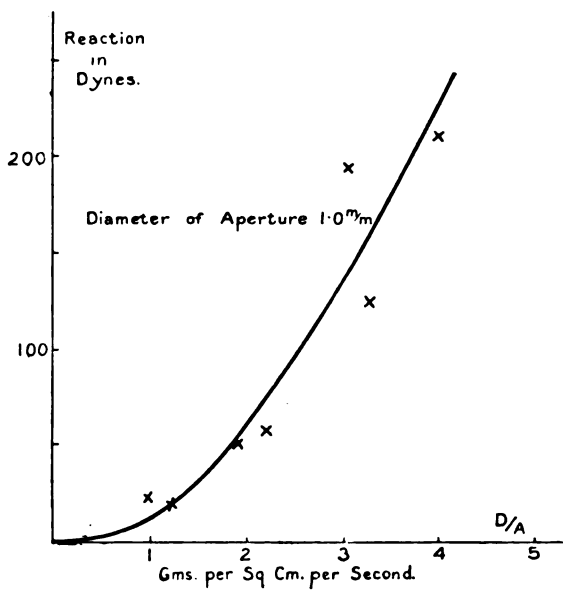


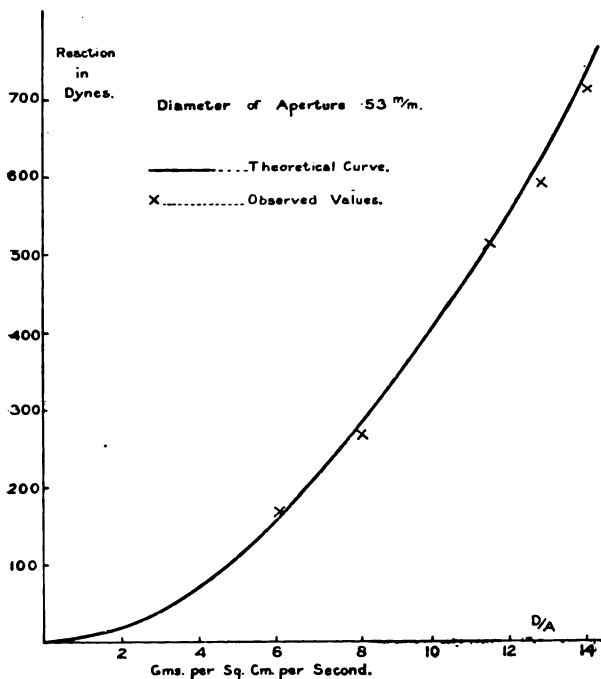
Fig. 6.



between theory and experiment. Numerical values are given in Table III., Appendix, Section 7.

The above comparison indicates that our theory satisfactorily explains the behaviour of steam issuing from an orifice under pressures varying from $1/4000$ to $1/3$ of an

Fig. 7.



atmosphere. We next proceed to test our equation for the high rates of discharge and high boiler pressures examined by Rosenhain. For the first two or three observations we take $\mu = 0.033$ as before, but after these the value of D

becomes so large that the factor $e^{-\mu \frac{D}{A}(r+1)}$ becomes negligible; β is then practically equal to unity, which means that all the external momentum is absorbed before it reaches the aperture; the curve then approximates to

$$R = Dv_i - \Pi A. \quad \dots \quad (15)$$

We have shown in Section 7, Table III. (note), how the value of v_i has been determined, so we may calculate the values of R for different values of D/A ; these are represented by the full line in fig. 3, the experimental values are shown by crosses, and again the agreement is very good. Thus our

equation proves satisfactory over a range of reactions varying from 6 dynes (as in fig. 4) to over 10^6 dynes (as in fig. 3), the corresponding rates of discharge varying from 0.2 to over 150 gms. per sq. cm. per second. Is it possible that such a measure of agreement can be accidental? *

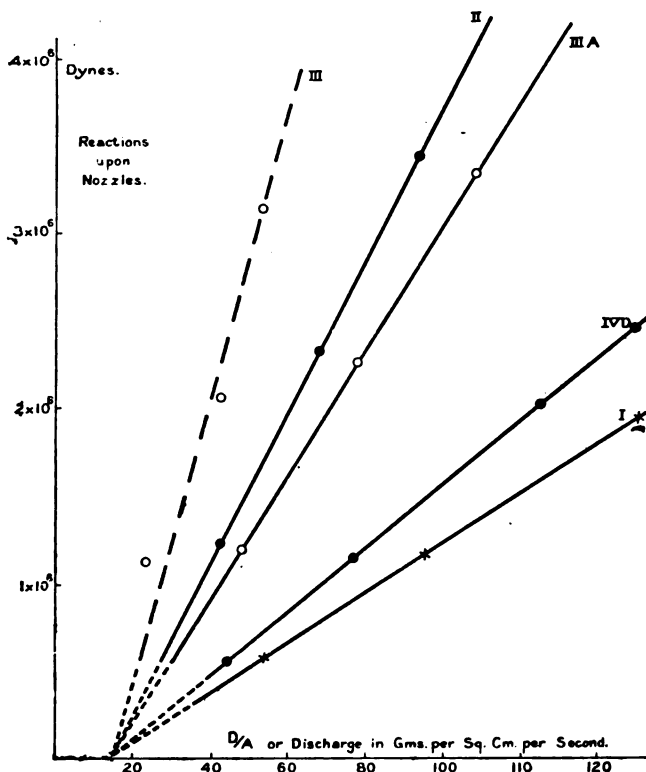
We may here draw attention to three interesting features of these researches:—(1) We saw on p. 647 that, on the supposition that a surface was discharging molecules into a vapour at the same temperature ($r=1$) and that each molecule approaching the surface was effective in neutralizing the momentum of an issuing molecule ($\beta=1$), it should be possible to attain a rate of discharge of approximately 15 gms. per sq. cm. per second without incurring a reaction above that of the atmospheric pressure; we saw also that this was the condition determining that twice as many molecules left the surface as would ordinarily have been incident upon it. It would be interesting to test this experimentally, but unfortunately the conditions are not capable of realization in practice, because for low discharge rates, when $r \approx 1$, every external molecule does not succeed in colliding effectively with one of the projected molecules, *i. e.* β is not unity; and also because, if we were to attain such a high rate of discharge that $\beta=1$, we could not do so without increasing the temperature of the interior, when r becomes greater than 1. We may, however, note that for the highest rates of discharge shown in fig. 3, for which β is nearly equal to unity, the points of observation lie very approximately on a straight

* [The agreement is certainly greater than might have been expected in view of the incomplete data available for the high pressure work, in the reduction of which we have had to make certain approximations referred to in the note attached to the Table recording them (Section 7, Appendix). If we had attributed to v_l the mean value instead of the R.M.S. value of the molecular velocity, the agreement would have been less good by about 8 per cent. for the highest rate of discharge, but, as we have stated, there seemed a definite reason for regarding the mean value as being too low; how much higher to take it we did not know, and we ought not to claim more than that it was a good guess to have taken it as the R.M.S. value, since that makes the agreement practically perfect over the whole range. We may note, however, that the matters referred to in the next two paragraphs are independent of the precise value assigned to v_l in the high pressure work.]

We had not hoped to show more than that the general phenomenon of evaporation and discharge was of the nature we have described—there must be other factors to be superposed upon our main theory. We should, for example, expect a small effect due to the priming of the steam, to the flow of vapour near the edge of the orifice, and perhaps to the presence of associated molecules in the escaping vapour. But it would seem that these effects are small compared with those which constitute the main lines of the Argument.]

line, as we should expect from equation (12), Section 8, since v varies but slightly. If we produce this line, which represents the condition $\beta=1$, backwards until it cuts the horizontal axis, we arrive at the point for which $\beta=1$, $r=1$, and $R=0$, and consequently realize, by extrapolation, the conditions we have imagined. For this point we note that D/A is very approximately equal to 15 gms. per sq. cm. per second, in excellent agreement with our simple theoretical conclusion.

Fig. 8.



It is interesting to find that not only does the aperture in a thin plate give a curve whose asymptote cuts the horizontal axis at $D/A=15$, but also that nozzles of various lengths, diameters, and tapers agree in giving this value to a very considerable degree of accuracy. Particulars of the nozzles used by Rosenhain and the reactions experienced at different discharge rates are given in Table IV., Section 7. The results are plotted in fig. 8. We are only concerned with

those portions of the curves for which $\beta=1$, *i. e.* with those parts which are appreciably straight. Drawing the asymptotes we find two things: first, that all, with the possible exception of that for nozzle III., converge towards a point on the axis; and secondly, that this point corresponds to $D/A=15$ gms. per sq. cm. per second. In view of the fact that the nozzles possessed tapers varying from 1 in 30 to 1 in 12, and areas which varied from 0.177 sq. cm. to four times that area, the result is a remarkable one. In the writer's opinion it would be difficult to account for it on any theory other than that outlined in the preceding pages. In other respects, however, our formula does not apply to expanding jets.

(2) The second point of interest is this:—We can easily show that the asymptote to the theoretical curve in fig. 3 produced backwards cuts the vertical axis at a point corresponding to -10^6 dynes per sq. cm. excess pressure, which is the same as zero, absolute, pressure. Consequently, points on the asymptote represent relationships which would have been obtained if the external medium exerted no pressure. Since the theoretical curve is experimentally indistinguishable from its asymptote a little before the first experimental point (which was obtained with a boiler pressure of 20 lb. per sq. inch) it appears that above this boiler pressure the rate of discharge is independent of the external pressure. It is thus satisfactory to find that our theory is in agreement with the well-recognized fact that the rate of discharge is independent of the external pressure when that pressure is less than half the internal pressure.

(3) We have pointed out that when the discharge rates are very small the effect of doubling the area of the aperture is to diminish the reaction by approximately one-half (*cf.* p. 652) for a constant value of the quantity discharged per second. This point is not an obvious deduction from equation (14) in its present form, but if we expand the exponential function, we may write it thus:

$$R = Dr_1 - 2\mu\Pi D + 2\mu^2\Pi D^2/A$$

if we confine our attention to small discharge rates for which r does not differ appreciably from unity. Since $r_1 = 6.6 \times 10^4$ and $2\mu\Pi = .066 \times 10^6$, we see that the first two terms on the right-hand side destroy one another, leaving

$$R = 2\mu^2\Pi D^2/A, \quad (16)$$

whence R is inversely proportional to the area, which is in accord with our observations. This, as we shall see by the

next Section, will hold good as long as the discharge is very small and takes place into a dense medium, and will be true for all vapours.

Internal Interference.*

Let us see if we can apply the foregoing investigation to obtain more detailed knowledge of the conditions governing the discharge of vapour from a liquid during the process of evaporation.

Consider the case of a saturated vapour above the mercury in a barometer tube. The vapour pressure is measured by the depression of the mercury below its normal level and is made up of the reaction due to the evaporation of molecules from the small stratum of liquid on the top of the mercury column and the impact of molecules from the vapour space. Unless the molecules are infinitesimal there is the probability of collisions between the two streams, so that all those with velocities directed downwards, which would have struck the liquid in the absence of evaporation, will not actually reach it, or, if they do, will impinge upon it with diminished velocity.

We have previously directed our attention chiefly to the effect of this interference upon the pressure upon the liquid—let us now consider the proportion of molecules in the vapour space which are prevented from reaching the liquid under conditions of saturation.

Since there is no loss of weight of the liquid, we have, in our previous notation, but writing β_i for the *internal* interference coefficient, and taking n_v as the number reaching the surface in the absence of *all* molecular projection from it:

$$L = n_i - n_v(1 - \beta_i) = 0. \quad \dots \quad (16 a)$$

Also the vapour pressure, R_v , is the pressure upon the surface and is given by

$$\begin{aligned} R_v &= mn_i v_i + mn_v(1 - \beta_i) v_v \\ &= mn_v(v + v_v)(1 - \beta_i), \text{ or since } v_i/v_v = r, \\ &= mn_v v_v(r + 1)(1 - \beta_i). \quad \dots \quad (17) \end{aligned}$$

We saw from equation (13 a) p. 658 that

$$\beta_i = 1 - e^{-\mu(r+1)mn_i},$$

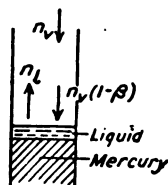
whence, from (16 a)

$$\beta_i = 1 - e^{-\mu(r+1)mn_v(1 - \beta_i)},$$

or, using (17),

$$\beta_i = 1 - e^{-\frac{\mu R_v}{v_v}} \quad \dots \quad (18)$$

* For definition, see Note, p. 658.



From our experiments with the suspended boiler we found the quantity μ for water vapour at atmospheric pressure to be $\cdot 033$. Since the temperature was 100°C ., $v_v = 6.6 \times 10^4$ cm./sec. and as $R_v = 1.01 \times 10^6$ dynes, it follows that $\frac{\mu R_v}{v_v} = \cdot 50$, whence $\beta_i = \cdot 393$. This means that at ordinary

pressures $\cdot 393$ of the momentum directed downwards is prevented from reaching the liquid.

A number of experiments were devised to measure μ for different liquids at their boiling-points, the apparatus already described and shown in fig. 1 being used. Electrical heating was substituted for the flame as some fumes were inflammable, and to avoid prolonged inhalation, the experiments were conducted within a draught chamber. The greater number were carried out by Mr. J. Webber, B.Sc. The results obtained are shown in Table II. The liquids used were carbon tetrachloride, ether, and alcohol in addition to water, which had previously been examined.

The value of μ was calculated as in the case of water vapour, and again we find a remarkable agreement in the values obtained for any particular substance for all rates of discharge. More remarkable, however, is the fact that at

the same atmospheric pressure the values of $\frac{\mu R_v}{v_v}$ are

practically the same for all these substances in spite of the differences in v_v consequent upon the different temperatures at which they boiled. The liquids had been chosen largely on account of their widely divergent molecular weights, which varied from 18 for water to 153.8 for carbon tetrachloride.

This discovery led to a suspicion that it might be a purely geometric result consequent upon the approximation of the experimental curve to a parabola; if these were parabolic throughout it might be substantiated, but the suspicion is dispelled by the fact that the curves are only parabolic near the origin; they soon definitely depart from this condition and become nearly linear, *vide* the points of observation in figs. 3 and 8. On the other hand, our formula is satisfied over the whole of the graph. It is more probable that the invariability of $\mu R_v/v$ is the property of a liquid which governs the conditions whereby it remains in equilibrium with its saturated vapour, or, in other words, it enables us to define the boiling-point in terms of the numbers of molecules directed towards and away from the surface.

TABLE II.

I. Experiments at Atmospheric Pressure.

Area of Aperture $\cdot 00754$ sq. cm. Diameter $\cdot 98$ mm.

Atm. Pressure dyncs.	Discharge per second.		Temp. of Vapour.	Molec. Velocity.	Ratio v_l/v_v .	Re- action obsd.			Mean value of $\frac{\mu R_v}{v}$.	β	
B _v .	D.	D/A.	T _{Abs.}	v_l .	r .		2μ .	$\frac{\mu R_v}{v}$.			
Carbon Tetrachloride CCl ₄ . B. Pt. 76°·7 C. Formula Weight 153·8.											
$\times 10^6$				$\times 10^4$							
1·018	·0295	3·91	...	2·185	1·0	28·1	·0209	·49	} ·49	·387	
1·018	·0537	7·12	348·8	"	"	114·0	·0208	·49			
1·018	·0470	6·22	348·7	"	"	74·8	·0212	·495			
1·018	·0650	8·62	350·0	"	"	161·0	·0207	·485			
1·018	·0918	12·18	350·8	"	"	300·0	·0206	·480			
1·018	·1586	21·1	352·0	"	"	[894·0]	[·0193]	[·45]			
Ether (C ₂ H ₅) ₂ O. B. Pt. 34°·6 C. Formula Weight 74·08.											
1·022	·0492	6·52	...	2·96	1·0	151	·0285	·49	} ·49	·387	
1·021	·01105	1·47	...	"	"	7·5	·0283	·49			
1·015	·0546	7·24	...	"	"	181	·0288	·495			
[1·010]	[·0548]	[7·27]	...	"	"	212	[·0277]	[·476]			
Alcohol C ₂ H ₅ OH. B. Pt. 78°·3 C. Formula Weight 46·05.											
1·010	·0716	9·53	351	4·01	1·0	506	·0389	·491	} ·49	·387	
1·012	·0345	4·57	"	"	"	142	·039	·492			
1·015	·0607	8·05	"	"	"	394	·039	·495			
Water H ₂ O. B. Pt. 106° C. Formula Weight 18.											
Mean of the first 27 observations recorded in Table III.										} ·50	·394
R _v the atmospheric pressure approx. $1\cdot 01 \times 10^6$ dynes											
μ , average value $\cdot 033$. $v_v = 6\cdot 6 \times 10^4$											
II. Experiments below Atmospheric Pressure.											
Ether.											
$\times 10^6$				$\times 10^4$							
·28	·0177	2·35	287·2	2·86	1·0	67·0	·0992	·49	} ·49	·387	
·64	·0113	1·50	300·0	2·92	"	13·3	·0454	·497			
·243	·0212	2·81	280·7	2·85	"	94·2	·116	·495			
·317	·02045	2·71	287	2·86	"	79·0	·087	·484			

We may note that the graph near the origin is parabolic at ordinary pressures because the probability of collisions is considerable and the exponential term important; at very low pressures we should expect to find it departing from this because the probability of collisions is small, so that both streams of molecules would independently affect the pressure.

Since $\frac{\mu R_v}{v_v}$ has the same value for all liquids tested, it follows that β_i will also be the same for each, provided of course that μ is always measured for temperatures and pressures which correspond to a condition of saturation. Also since $\beta_i = .393$, we have $n_l = n_v(1 - \beta_i) = .606n_v$.

Some caution is necessary in interpreting this:— n_l and n_v are numbers of molecules defined on the assumption that all possess the mean molecular velocity; it indicates that, in so far as it is legitimate to replace the actual velocity distribution by this conception, a smaller number are projected in each second than those with velocities in the downward direction. It is not, however, dependent upon any assumption regarding the relative velocities of the ejected and circumambient molecules since equation (18) does not involve r .

The ratio of n_l to n_v obtained above appears reasonable, because, since there is no loss of weight of a liquid in equilibrium with its saturated vapour, we have $n_l = n_v(1 - \beta)$. Moreover, since the number of vapour molecules stopped cannot be greater than the number rising, we have $\beta_i n_v \geq n_l$. Writing $\beta_i n_v = kn_l$, where k varies from 0 to 1, it follows that

$$n_l = n_v - kn_l, \quad \text{or} \quad n_l/n_v = \frac{1}{1+k}.$$

This ratio may clearly have any value between $\frac{1}{2}$ and 1. If the pressure is low we have such small densities that collisions are improbable, so $k=0$ and $n_l=n_v$; on the other hand, an increase of density is favourable for collisions and the limiting case occurs when $k=1$ and $n_l=\frac{1}{2}n_v$. This happens when all projected material is stopped and would only be likely at high pressures.

Fresh experiments were undertaken to find the variation of n_l/n_v with temperature and pressure. Mr. J. Burgess kindly gave me great assistance in these investigations.

A smaller and improved form of reaction boiler or Hero's engine was constructed and suspended within a bell-jar, so

arranged that by electrical heating the liquid within could be boiled. Ether was used. After one or two attempts we found it possible to measure μ for pressures varying from $1/4$ to 1 atmosphere. Though μ had proved to be a constant for a particular external pressure for all rates of discharge, it is now shown to be a function of the external pressure. One factor we had not taken into account in estimating the amount of interference between two opposing streams of molecules was the effect of further collisions upon those which had suffered effective collisions. Working backwards, it seems that, *for a given total number of encounters*, the chance of a collision being effective becomes less as the number of molecules in the external atmosphere increases. Possibly because subsequent encounters cause an associated pair to be resolved, or possibly because collisions are only effective when they occur between ejected molecules and newly evaporated material.

A very curious fact emerged from these experiments, which are also tabulated in Table II., namely, that, though μ varies with the pressure employed, the value of $\frac{\mu R_v}{v_v}$ remains

unaltered at the value we had previously found for water and other liquids at their boiling-points. It has never been found to differ very appreciably from $\cdot 5$. Since

$\beta_i = 1 - e^{-\frac{\mu R_v}{v}}$, we see that β_i for all saturated vapours examined has the value $\cdot 393$, and that $n_i/n_v = \cdot 607$.

It is not the writer's opinion that these quantities would prove to be universal constants for all saturated vapours at all pressures. If the experiments could be conducted under sufficiently high vacua, it seems almost inevitable that the ratio of n_i to n_v will approach unity. It is desirable, but difficult, to test this.

It is certainly very surprising to find no certain variation in β_i when the pressure undergoes a 4 to 1 change. We should not expect to find a stationary value until $n_i/n_v = \cdot 5$, when $k=1$ and all the projected material is effective in preventing the external momentum from reaching the surface. It would be interesting to find whether a statistical examination of our problem would alter our value of β_i from $\cdot 393$ to $\cdot 5$, which would be in accord with this point of view.

[Another possible modification of our problem also requires consideration. We have previously supposed that the β_{n_v} .

molecules which had been prevented from reaching the surface by collisions remained part of the vapour, but it is possible that some sort of binary system is formed which drifts back eventually to the surface and is to be added to the liquid. This would be in keeping with the simplification introduced into our mathematical treatment, namely, that interference operated through the complete stoppage of a few molecules, the rest maintaining their velocities unimpaired. It is interesting to note that on the assumption that binaries are formed, and that all fall back upon the liquid, equation (16 a) becomes

$$L = n_l - n_v(1 - \beta_i) - 2\beta_i n_v = n_l - n_v(1 + \beta_i) = 0,$$

and we should find $\beta_i = .632$ and $n_l/n_v = 1.632$, which is not an improvement upon our earlier estimate. If, however, only the projected material which suffers interference drifts back to the liquid, we have

$$L = n_l - n_v(1 - \beta_i) - \beta_i n_v = n_l - n_v = 0.$$

This gives us in place of equation (17)

$$R = mn_v r_v(r + 1 - \beta_i),$$

whence it follows that

$$\beta_i = 1 - e^{-\frac{\mu R_v}{v_v} \frac{r+1}{r+1-\beta_i}} = 1 - e^{-.5 \frac{r+1}{r+1-\beta_i}},$$

or, if $r=1$,

$$\beta_i = 1 - e^{-.5 \frac{2}{2-\beta_i}} = 1 - e^{-\frac{1}{2-\beta_i}},$$

an equation which is satisfied with considerable accuracy if $\beta_i = .5$, i. e. if half the material directed downwards is stopped by collisions.

We may note that our treatment of the jet experiments is not affected by this assumption, it is most improbable that any material condensed outside the vessel will re-enter it.]

It thus seems that when a liquid is in equilibrium with its saturated vapour, there is always a definite ratio between the number of molecules issuing from the surface and those directed towards it; this ratio is .607 (or possibly 1). As the boiling-point is defined as the temperature at which the vapour pressure of the liquid is equal to that of the

surrounding atmosphere, we may define the boiling-point as that temperature at which the emission is such that $\cdot 393$ (or possibly $\cdot 5$) of the downward momentum is prevented from reaching the liquid by the shielding action of the projected material. At a higher temperature for a given pressure, the emission increases and more molecules leave than enter the liquid, which therefore boils away ; at a lower temperature the emission is less and there is condensation.

One consequence of the invariability of $\mu R_v/v$ is that we may apply it to equation (16) when, since the discharge is small, the pressure of the vapour in the boiler will be nearly equal to the external pressure, *i. e.* $R_v = \Pi$, so that by substituting for μ from the equation $\mu \Pi/v_l = \cdot 5$, we have for the total reaction, R , upon a vessel with an aperture of area A

$$R = (Dv_l)^2/2\Pi A,$$

which is a great simplification of equation (14); it holds good with considerable accuracy, but is, of course, only applicable to small rates of discharge. We are, however, now in a position to predict the reaction experienced by an orifice of any small area A in a thin plate for all discharge rates and for all liquids which behave like those we have examined. We can find μ for the particular liquid, external pressure, and boiler temperature from the above equation ; knowing D and obtaining v_l from the kinetic theory, we can at once calculate R from equation (14).

In conclusion, I wish to thank Professor J. W. Nicholson, F.R.S., for his continued interest in this research and for his encouragement to publish it. I am also indebted to Dr. Harold Jeffreys for reading it through ; I do not think there is anything in it at variance with his own treatment of evaporation. I have mentioned in the text the members of my own laboratory, Messrs. H. Tunley, J. Webber, and J. S. Burgess, to whom I am very grateful for willing assistance.

University College,
Reading.

PART II.

APPENDIX.

TABLE OF SECTIONS.

SECTION	PAGE
1. Experiments upon liquids evaporating into the open air	672
2. Note upon the mechanism whereby a boiling liquid discharges its vapour	673
3. Experiments upon liquids boiling in the open air ..	674
4. Note upon the velocities of molecules evaporating from a liquid surface	675
5. Experiments upon a liquid evaporating <i>in vacuo</i> ..	676
6. The velocities of molecules discharged from an orifice in a boiler under steady conditions	678
7. Experiments upon the reaction consequent upon the emission of steam from a boiler	679
8. Theoretical considerations relating to the phenomenon of evaporation	684
9. Theoretical considerations relating to the efflux of vapour molecules from a boiler under steady conditions	687
10. Previous experiments bearing upon an evaporative reaction	688

SECTION I.

Experiments upon liquids evaporating into the open air.

(Vide Part I. Argument, page 643.)

IN the two pans of a balance similar crystallizing dishes were placed, one containing ether, and the other counterpoise weights. Each was provided with a cover-glass, that over the ether being ground to fit tightly: these were made equal in weight by pasting strips of paper on the lighter one. Balance being obtained, the two covers were removed, when the ether began to evaporate. The motion of the pointer was watched. After one minute the covers were replaced and weights added to restore the balance and to measure the amount of ether which had evaporated in the interval. In a typical experiment the rate of evaporation, D , was 0.00133 gm. per sec., the temperature was $15^{\circ}\text{C}.$, hence the molecular velocity, v , was approximately 4×10^4 cms./sec., whence, assuming normal projection, the rate of loss of momentum $= Dv = 52.5$ dynes $= 0.054$ gm. weight. From the measured rate of loss of material 0.054 gm. would evaporate in 41 seconds: consequently, if there were no compensating action, the pan containing the liquid should have been depressed until 41 seconds from the beginning of the experiment. Observation showed that from the

start this pan rose, consequently we conclude that there is no such unbalanced pressure under the conditions of the experiment. The balance was easily sensitive to 0.001 gm. Other experiments carried out in the same manner gave similar results.

SECTION 2.

Note upon the mechanism whereby a boiling liquid discharges its vapour.

At first it seemed doubtful whether the projection of molecules from a boiling liquid could be usefully examined. The bubbles originate at the base of the liquid and rise to the surface; if, as is generally held, they then burst and discharge their vapour into the space above the liquid, we could not regard the molecules as crossing the surface with anything approaching their temperature velocities, but close examination of the process does not confirm this view of the manner in which the vapour escapes. Only a very small fraction of those which reach the surface burst, the bulk of them appear to part with their vapour by a process akin to diffusion through their enclosing skins—perhaps by evaporation from their exterior surfaces accompanied by condensation of the vapour within. At any rate they gradually subside to the general level of the liquid; this is true even for the large bubbles formed by the coalescence of several small ones; it is rare for one to burst.

The phenomenon has been carefully watched in shallow and in deep vessels, and I am indebted to Mr. H. Tunley and Mr. J. Webber for checking this observation with me. The phenomenon was well shown by water boiled in the shallow lid of a square tin in which the liquid bulged high over the edges. The bubbles rose chiefly at the corners where many coalesced into large bubbles. These then floated towards the centre, growing gradually smaller until all that was left there was a froth of tiny bubbles. In a typical experiment the surface lost 0.0015 gm. per sq. cm. per second, which is a rapid rate for boiling in the open and I doubt if a single bubble burst when the surface was convex.

When the vessel is deep the bubbles rise in a stream and sometimes float on the surface, but frequently condensation takes place a little below the surface; the motion occasions a pronounced convexity which increases the surface area, and therefore the amount of evaporation. In this way a balance is arrived at between the rates at which heat is

Phil. Mag. S. 6. Vol. 45. No. 268. April 1923. 2 X

applied and removed from the liquid. Sometimes minute droplets are thrown 4 or 5 inches above the liquid and then fall back; they do not appear to be due to condensed vapour, but to a jerking upwards of the liquid above a string of rising bubbles which collapse suddenly.

Blowing upon a bubble-strewn surface does not cause them to burst, but stops their formation below the point towards which the stream of air is directed. Bubbles of dissolved air burst when they reach the surface.

The last stage in the boiling of water in a smooth tin is the formation of a layer of water in a thin skin at the bottom, this evaporates without bubbling, even though ebullition may have been brisk when the water was deep.

SECTION 3.

Experiments upon liquids boiling in the open air.

Since we have shown in the Argument that no delicate experiments were required in the first instance, the investigation of a possible recoil was made in much the same way as before, water being boiled on the scale-pan of a balance and the motion of the pointer observed. A flame was first applied below an empty pan and balance obtained; a small quantity of water contained in a tube was then suspended above this pan and a counterpoise placed in the other pan. It was arranged that when a wax plug in the bottom of the tube melted, the water would flow out on to the pan, where it should at once begin to boil. Any resultant reaction would be measured by a downward motion of the pan, allowance being made for the rate at which it lost weight and for convection and allied effects.

In an actual experiment 5.5 gms. of water boiled away in 3 minutes, whence, as we have seen, the quantity Dv is equal to the weight of 2.14 gms. (or 1.23 gms. if the projection is at random instead of normal); though the pointer showed small oscillations as it gradually moved in accordance with the rate at which weight was being lost, no oscillation corresponded to a pressure upon the surface as great as 0.1 gm. weight. Had there been an unbalanced reaction due to the molecular projection, the pan containing the liquid should have been depressed by a force varying from not less than the weight of 1.23 gms. at the outset to zero 40 seconds later.

In a second experiment a more sensitive test was provided, the water was contained in a small test-tube, which was

held in a vertical position by a thread ; balance was obtained with a flame below the pan and the cotton burnt ; the water then spilled on to the pan and quickly boiled away. The pointer of the balance showed a continuously increasing downward tip of the other pan. The mass of the water was 3.20 gms. and this boiled away in 20 seconds, the rate of loss being 0.16 gm. per second. The quantity Dv has the value 1.12×10^4 dynes, which is equivalent to the weight of 11.4 gms., a quantity more than 3 times greater than the whole weight of water, a force which could not have escaped observation if it were in operation and unbalanced, and which should have persisted until all the water had boiled away. Preliminary experiments had shown that the displacement of the little tube, when the cotton was burnt, did not disturb the balance appreciably, and that convection currents provided no effect comparable with the magnitude of Dv .

SECTION 4.

Note upon the velocities of molecules evaporating from a liquid surface.

As we have stated in the outline of the Argument a conceivable explanation of the absence of a reaction upon an evaporating surface is that the molecules issue with zero or very small velocity. We might imagine that the molecule in the liquid state possesses just sufficient energy to carry it clear of the surface, where it remains at the absolute zero of temperature or with very small velocity until it is swept away by the vapour above and caused to share in the general motion of the rest of the molecules. The energy necessary to produce this motion would presumably be derived from the vapour, which would receive the equivalent heat from contact with, or radiation from, the hot liquid or the sides of the vessel.

This view is far from the usual interpretation of the phenomenon of boiling or evaporation, but it is difficult to quote any quite conclusive argument against it. Since distillation can take place in a vacuum it seems improbable, but provided the molecules issue with just sufficient energy to carry them clear of the surface, we could understand the liquid losing weight. The strongest argument against it lies, I think, in Knudsen's experiments (*Annalen der Physik*, xlvii. p. 697 (1915)), in which he observed the rate of evaporation of a drop of mercury *in vacuo*, and found that it agreed with a formula derived from the kinetic theory on

the assumption that evaporation was the reverse process of condensation, and, therefore, that the molecules escaped with the velocity of the vapour molecules at the same temperature. The formula had previously been obtained by Langmuir.

The writer thought it possible to test this matter further, so devised some experiments whereby it was sought to investigate the character of the reaction upon a surface evaporating in a vacuum. If evaporation from such a surface were suddenly permitted, it seemed that the reaction should attain its maximum value instantaneously if the molecules escaped with their molecular speeds, but that if they merely "dropped off," it would take an appreciable time for the molecules to acquire velocities appropriate to the temperature by radiation or contact with the sides of the vessel, or, in other words, that their vapour pressure would take an appreciable time to develop.

The apparatus described in Section 5 was employed, and it is sufficient here to say that (1) a reaction of a powerful nature was observed, and (2) that it appeared to be of a sudden explosive character, as though the molecules were projected with initial speeds of great magnitude.

The accumulated evidence is thus, in the writer's opinion, in favour of molecular projections with high velocities, though whether these are appropriate to the temperature as given by the kinetic theory was not determined. As far as our evidence goes it favours Knudsen's view. We may, however, note that the precise value of the velocity does not enter into our final equations dealing with the phenomena of evaporation.

SECTION 5.

Experiments upon a liquid evaporating in vacuo.

The experiments devised to observe if there is any recoil *in vacuo*, and referred to in Section 4 and on p. 649 *et seqq.* of the Argument, were carried out as shown in fig. 9. Fig. 10 shows a larger scale elevation of the tap A. The experiment consisted in filling the hole drilled through this tap half with mercury and half with water when the tube was vertical, and then turning it round until the tube was horizontal, when both ends were simultaneously thrown into communication with the tubes B and C, which were connected to the equally exhausted reservoirs D. If the molecules possess sensible velocities of escape they will occasion a reaction upon the liquid surface, which will result

in the expulsion of the mercury from the tap into the tube B. Preliminary experiments showed the importance of eliminating any layer of air in the interface between the mercury and the water, because if it is present, the mercury will go off in one direction and the water in the other. To get rid of the air, the water and the mercury were first boiled separately and then brought together in a reservoir below F.

Fig. 9.

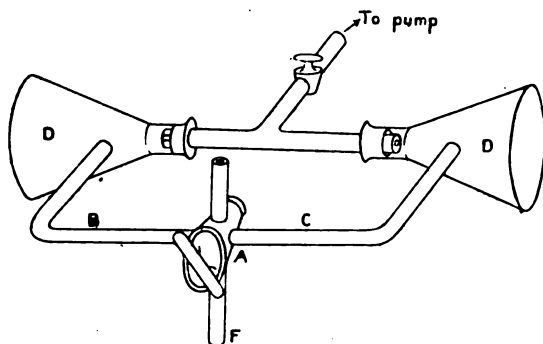
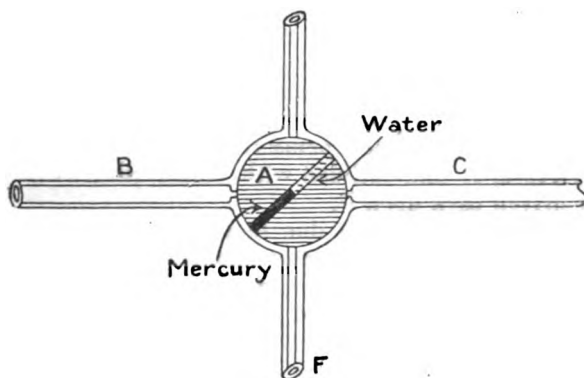


Fig. 10.



This was boiled so that steam filled the tube F and the tap, and finally, when the tube was thus as free from air as possible, the water and mercury were sucked up into the tap until it was half full of both; the tap was then turned through 45° , while DD were exhausted. On turning tap A quickly until the tube through it was horizontal, the behaviour of the mercury was observed.

With one exception, possibly due to a leak in the tap, a large number of experiments agreed in showing a recoil of

the mercury in the direction to be expected if the molecules were projected from the water with high speeds. It had been hoped to obtain an accurate measure of the pressure at which the recoil first became apparent, but an improved form of the apparatus ordered twelve months ago has not yet been delivered, so this extension of the investigation has been postponed.

The feature of the experiment was the sudden, explosive character of the reaction, the mercury being blown violently into the tube behind it, sometimes being shattered into a number of small drops.

In devising the experiment it had been assumed, apparently with justification, that the rate of evaporation of mercury at the temperature of the experiment would be negligible compared with that of water.

In Section 10 is quoted an experiment carried out by Osborne Reynolds which, as he interprets it, seems to indicate that at pressures below about 2.5 mm. there is a reaction when water evaporates.

SECTION 6.

The discharge of molecules from an aperture in a boiler.

The apparatus used to test the reaction due to the projection of steam from an aperture was of such a form that the molecules, which were originally emitted vertically from the horizontal surface of a liquid, escaped horizontally from an aperture whose plane was vertical. Thus all molecules which escaped had either themselves struck the side opposite the aperture, or had collided with others which were themselves driven back upon it.

As far as the reaction due to the escaping molecules is concerned, we may thus regard a small area of the opposite wall as the emitting surface, and, since we are only concerned with the component of the molecular velocity normal to the aperture, we may regard this area as the geometric shadow of the aperture itself.

Any interference which takes place between the issuing material and that incident from outside will occur somewhere along the jet based upon this small area, and may happen either within, or, more probably, outside the vessel. Along this jet it should be possible to find some section which serves as the boundary between regions in which interference does and does not take place, it marks the limit to which the external molecules can penetrate and still be liable to interference; all external molecules which succeed in reaching

it will affect the reaction experienced by the vessel in the ordinary way. This may be the wall itself or a plane near the aperture, or even some section beyond the aperture. We shall designate this section the "effective aperture" of the vessel. Our object in defining it is to indicate that it corresponds to the surface of an evaporating liquid so far as our particular problem is concerned.

We may note that if the effective aperture is within the vessel, it is probable that external vapour molecules will be condensed within it, whereas, if it is outside, such molecules will not necessarily, or even probably, be captured, though their momentum cannot fail to be conveyed by elastic collisions to the opposite wall.

The problem of the discharge of steam from such a vessel is thus very similar to the projection of molecules from a liquid in the process of evaporation. In the former, the molecules which pass outwards through the effective aperture will have occasioned a reaction upon the opposite wall given by their mass multiplied by the normal component of their molecular velocity, and the total force upon the vessel is compounded of this reaction, together with that due to the incidence of the external atmosphere after it has suffered encounters with the issuing stream.

There may, however, be differences in the distributions of the velocities of the discharged molecules about the normals to the evaporating surface and the aperture respectively; at present we make no assumptions concerning them. We may note, however, that from an investigation upon quite different lines, Knudsen (*Annalen der Physik*, xlvii. p. 697 (1915)) finds that the evaporation of molecules from a liquid surface *in vacuo* is equivalent to the efflux of gas molecules from an aperture of the same dimensions. In the writer's opinion the resemblance extends to discharges into the atmosphere.

SECTION 7.

Experiments upon the reaction consequent upon the emission of steam from an orifice in a boiler.

The experiments were performed with a piece of apparatus of the general form of Hero's engine:—a cylindrical brass vessel 3.1 cms. internal diameter was provided with four radial arms (7.5 cms. to centre) as shown in fig. 1. It contained water and was heated by a flame below it.

Steam issued tangentially and provided a torque which was measured by noting the twist given to a torsion fibre, a

circular scale being attached to the apparatus and read against a fixed pointer. There was at first a good deal of irregularity in the rate of boiling, so it was necessary to take the mean of a large number of swings on both sides, but with experience, the amplitudes of the oscillations were greatly reduced. The apparatus was weighed cold before and after each run, so that the rate of loss of steam could be determined.

A thermometer with its bulb in the steam gave the temperature, and in some experiments a U-tube gauge was used to give the pressure, but when the excess within was small this could not be determined with much accuracy. The apertures were holes drilled in thin sheet brass, and between experiments were varied in number and size.

Convection currents were found to produce no appreciable effect. After the flame was applied, but before the steam issued, the pointer remained at zero. It also returned to zero immediately the flame was removed and steam ceased to escape, though the apparatus was still very hot. While steam was actually issuing no variation of the reaction could be produced by screening the rear parts of the arms from which the steam issued; also, as we have stated, the introduction of an obstacle within 2.5 mm. of the orifice and within the jet had no effect.

The first experiments related to the efflux of steam from the four apertures fully open, when the sum of their areas was equal to that of the cross-section of the central tube in which the water was boiling. The temperature of the steam in the orifice was sensibly the same as that immediately above the liquid. The first three experiments quoted in Table I. show that the observed reaction was either zero or differed from zero by a negligible quantity. In order to show that the interactions with the atmosphere are of great importance, we may contrast this with the rate at which the vessel was losing momentum from the escape of vapour molecules on the supposition that this is the only factor. We have already indicated that the velocity of rebound from the wall opposite the aperture previous to escape is of the order of magnitude of that with which the molecule leaves the liquid: consequently the rate of change of momentum on the assumption that the jets are parallel, which is not quite the case, may be calculated from the quantity Dv , where D is the number of gms. discharged in one second, and v is of the order of 7×10^4 cms. per second for steam at 100°C . Thus in the three experiments the

deflexions which would have been occasioned by these forces, if there were no compensating action, would have amounted to 6300° , 32000° , and 9510° respectively. Since in the actual experiments the deflexion was sensibly zero, we must conclude that in this case, as in the evaporation experiments, the outgoing molecules encountered the molecules of the external medium, which were advancing towards the aperture, and prevented them from reaching the vessel and communicating their momenta to it. These experiments may be said to confirm our view of the interference of the two streams of momentum.

The remaining observations recorded in Table I. show that as the number of apertures was reduced from four to one a reaction upon the vessel was observed, but that it was always very small. It is, however, clear that we must reduce our aperture if we wish to increase the reaction for a given rate of discharge.

Table III. records a number of experiments made by Mr. Tunley and the writer using small orifices varying from $\cdot 1$ to $\cdot 6$ cm. in diameter, and also deals with a special set by Mr. Burgess and the writer made upon an orifice only $\cdot 05$ cm. in diameter.

Data for higher rates of discharge are available from a series of experiments conducted by Rosenhain in 1900, in an investigation upon nozzles used in steam turbines; his experiments were carried out on a large scale, with an aperture of $\cdot 475$ cm. in a thin plate, the steam being produced in an engine-boiler under pressures up to 200 lb. per sq. inch. The steam escaped in a horizontal jet from a chamber suspended by a flexible tube, the reaction being measured by means of a weight attached to a cord passing over a pulley, which gave the chamber a horizontal thrust.

The rate at which steam was discharged was ascertained by condensing it in a vessel surrounding the jet. Though the object of the experiments was entirely different from that of those under discussion, it is possible to derive the necessary data from cross reference to Rosenhain's diagrams. This is given in the final section of Table III. Attention is for the present drawn to the observations and quantities deduced directly from them; the calculated values will be discussed later.

Table IV. records observations made by Rosenhain when nozzles of various forms were substituted for the orifice in a thin plate.

TABLE III.

Observers : J. S. Burgess, H. Tunley, G. Duffield.

No. of Apertures.	Diam. of Aperture.	Dis-charge per second. D.	Dis-charge per sec. per unit area. D/A.	Temp. of steam. T _{Abs.}	Molecular velocity. v_L	Ratio v_L/v_{100} . r.	Reaction observed. dynes. R _o .	Reaction calculated. dynes. R _c .
1	53 mm.	{ .0133	6.03	374.5	6.60×10^4	1.0	167	165
		{ .0180	8.2	376.0	6.61	1.00	267	285
		{ .0256	11.6	379.5	6.66	1.01	519	522
		{ .0283	12.8	379.6	6.67	1.01	590	632
		{ .0308	13.95	382.0	6.72	1.02	715	735
1	1 mm.	{ .0076	.96	373	6.60	1.0	22	12
		{ .0094	1.19	"	"	"	18	20
		{ .0149	1.89	"	"	"	51	56
		{ .0178	2.26	"	"	"	60	78
		{ .0260	3.30	"	"	"	125	155
1	2 mm.	{ .0239	3.03	"	"	"	195	140
		{ .0313	3.97	"	"	"	212	230
		{ .0088	.28	"	"	"	5.6	6
		{ .0099	.31	"	"	"	6.2	9
		{ .0180	.57	"	"	"	22	27
1	3 mm.	{ .0255	.82	"	"	"	45	46
		{ .0334	1.06	"	"	"	75	76
		{ .0380	1.21	"	"	"	109	100
		{ .0420	1.34	"	"	"	133	120
		{ .0443	1.41	"	"	"	133	138
1	4 mm.	{ .0500	1.59	"	"	"	172	180
		{ .0124	.18	"	"	"	6.2	6
		{ .0220	.31	"	"	"	17	16
		{ .0237	.34	"	"	"	19	18
		{ .0310	.44	"	"	"	36	33
1	5 mm.	{ .0330	.47	"	"	"	42	38
		{ .0559	.79	"	"	"	122	106
1	4 mm.	{ .0326	.26	"	"	"	20	
1	5 "	{ .0351	.18	"	"	"	16	
1	6 "	{ .0358	.13	"	"	"	15	
2	1 "	{ .0206	1.31	"	"	"	58	
2	2 "	{ .0470	.75	"	"	"	89	
2	2 "	{ .0359	.57	"	"	"	42	
3	2 "	{ .0199	.21	"	"	"	10	
3	2 "	{ .0390	.41	"	"	"	49	
4	2 mm.	{ .0344	.27	"	"	"	21	
		{ .0370	.29	"	"	"	23	
		{ .0333	.23	"	"	"	20	
		{ .0275	.19	"	"	"	15	
		{ .0271	.13	"	"	"	14	
		{ .0245	.12	"	"	"	12	
		{ .0209	.07	"	"	"	6	
		{ .0417	...	"	"	"	19	
		{ .0480	...	"	"	"	18	
		{ .0320	...	"	"	"	5	

TABLE III. (cont.).
High Pressure Discharge (Rosenhain).
Diameter of Aperture 4.75 mm.

Boiler Pressure lb. per sq. in.	D.	D/A.	T _{calc.}	v_l	r .	R _{obs.}	R _{calc.}
20	6.1	34.5	309	7.46×10^4	1.04	$.29 \times 10^6$	$.29 \times 10^6$
40	9.7	54.7	415	7.60	1.06	.58	.56
50	11.3	63.9	421	7.66	1.07	.73	.69
100	20.3	114.5	443	7.86	1.10	1.44	1.41
150	28.0	158.0	459	8.0	1.12	2.08	2.05
200	(35.4)	(200.0)	471	8.1	1.13	(2.82)	2.67

Note upon Table III. :—

(1) *Low pressure experiments.*—Though the application of the quantities recorded in the Table is reserved for later discussion, we may state here the manner in which they were evaluated.

D was found by weighing, as described in the text. The diameter of the 0.53 mm. orifice was obtained with the help of a travelling microscope; the other orifices were less carefully measured. The temperatures were those given by the inserted thermometers after correcting for stem-exposure, etc. Only in the case of the 0.53 mm. aperture did this differ appreciably from 373° Abs.

The molecular velocity was calculated from the formula

$$\bar{V} = 18.4 \times 10^4 \sqrt{\frac{2}{18}} \sqrt{\frac{T}{273}},$$

and the value of v_l taken as $.921 \bar{V}$, so that in the low-pressure experiments it is the mean velocity of the molecule.

In calculating r , the ratio of the velocity of the escaping molecules to that of those outside, the external medium was taken to be steam at 100° C.; it is difficult to be sure of this, but the value of r is not a very important quantity in our subsequent equations. Upon no reasonable assumption could it differ greatly from unity.

(2) *High pressure experiments.*—Unfortunately Rosenhain's published data are incomplete (Proc. Inst. C. E. vol. cxl. pt. ii., 1899–1900), and our measurements have been taken from his diagrams. The boiler temperatures are not stated, so we have estimated them on the assumption that the steam was saturated vapour at the given boiler pressure by using steam tables. But it is probable that the temperature was a little higher than the value thus obtained, because, since steam was escaping rapidly, the measured pressure was probably less than that of stagnant saturated vapour corresponding to the actual temperature. We have calculated $\bar{V}$ as before, but v_l has been given the R.M.S. value, instead of the mean value, as was done when the temperature was actually observed.

TABLE IV.
The Reaction upon Nozzles (Rosenhain).

Nozzle.	Length.	Maximum Aperture. sq. cms.	Taper.	Boiler Pressure in lb. per sq. in.									
				200		140		80		40		20	
				R.	D/A.	R.	D/A.	R.	D/A.	R.	D/A.	R.	D/A.
I ...	0	·177	none	$\times 10^6$ 2·82	(200)	$\times 10^6$ 2·0	151	$\times 10^6$ 1·15	94·5	$\times 10^6$ 0·58	54·7	$\times 10^6$ ·29	34·5
II ..	5·3	·417	1 in 20	3·44	94·8	2·35	68·6	1·22	42·5	0·49	12·0	·22	5·45
III ...	5·5	·686	1 in 12	3·15	53·5	2·07	43·0	1·11	23·8	0·33	13·9	·16	8·6
III A.	2·0	·329	1 in 12	3·30	109	2·24	78·5	1·18	48·3	0·49	27·6	·20	17·9
IV D.	1·7	·212	1 in 30	2·88	171	2·05	125	1·16	77	0·53	4·5	·22	(21·4)

The nozzles were of the expanding type. The inlet edges of III, III A, and IV D were slightly rounded.

SECTION 8.

Theoretical considerations relating to the phenomenon of evaporation.

We proceed next to consider in more detail the conditions which determine the pressure upon an evaporating surface.

The pressure is made up of two parts: (a) that due to the impact of molecules of vapour from above—we shall assume in the first instance that the external medium close to the surface consists entirely of the vapour of the liquid; and (b) that due to the rate of loss of momentum from the evaporating surface.

Let n_v be the number of vapour molecules which, if there were no loss by evaporation from the liquid, would strike a unit plane area within the vapour space close to the liquid in one second, let v_v be the mean velocity component of these molecules normal to the surface, and m the mass of each; then the pressure upon unit area Π due to these is given by the momentum delivered in each second, namely

$$\Pi = 2mn_v v_v. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If now evaporation takes place, it is clear that the momentum of which we have been speaking will encounter an opposing stream of rising molecules, and that collisions

will tend to reduce the number penetrating to the surface. Some of the molecules will have their velocities reduced to zero, so that they do not reach the surface at all.

Let us regard the loss of momentum of the downward stream as equivalent to the complete stopping of a fraction β of the original n_v molecules.

Thus the number of molecules actually reaching the liquid is $(1-\beta)n_v$; of these let the fraction α be reflected, so that the number penetrating the surface is $n_v(1-\beta)(1-\alpha)$. Since it is possible that the surface discriminates between fast and slow moving molecules, let us write v_v' for the normal component of the velocity of those which penetrate it, and v_v'' for those which do not.

Let n_l molecules leave unit area of the surface per second on account of the evaporation process, and let v_l be their mean velocity component normal to the surface. Then the number of molecules, L , permanently lost by each unit of area in one second is the difference between n_l and those which penetrate the surface, or

$$L = n_l - n_v(1-\beta)(1-\alpha). \quad (2)$$

When a liquid is evaporating freely into the atmosphere, for example from the pan of a balance, the conditions close to the surface are as represented in the accompanying

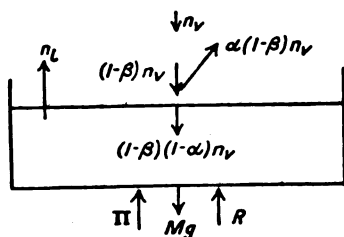


figure. Here R is the applied force necessary to secure equilibrium, and Π the pressure of the atmosphere acting upwards upon the base of the pan. The arrow marking n_v is supposed to be sufficiently removed to be free from the effect of the rising molecules.

Let Mg be the weight of the vessel and its contents at any instant, then, since each escaping molecule contributes to the resultant downward pressure a quantity mv_l , each molecule reflected from the surface an amount $2mv_v''$, and

each molecule which penetrates the surface an amount mv_v' , we have

$$R + \Pi - Mg = mn_l v_l + 2\alpha(1-\beta)mn_v v_v'' \\ + (1-\beta)(1-\alpha)mn_v v_v'. \quad \dots (3)$$

The natural limits between which α and β may lie are 0 and 1, but the available evidence for a clean surface indicates that $\alpha=0$ (Bennewitz, *Annalen der Physik*, lix. p. 193 (1919); Knudsen, *ibid.* xlv. i. p. 697 (1915)). Accepting this value, it follows that $v_v = v_v'$, since the whole of the advancing stream of momentum $m(1-\beta)n_v v_v$ penetrates the surface. Substituting these values for α and v_v' , it follows that

$$R + \Pi - Mg = mn_l v_l + (1-\beta)mn_v v_v, \quad \dots (3a)$$

or, since we may suppose the instantaneous value of Mg to be balanced by a weight in the other pan, we have, if we substitute for Π from (1)

$$R = mn_l v_l - (1+\beta)mn_v v_v. \quad \dots (4)$$

Also from (2)

$$L = n_l - (1-\beta)n_v. \quad \dots (5)$$

It is not possible to observe n_l directly, but, using its value as given by (5) in (4), we obtain

$$R = mLv_l + mn_v(1-\beta)v_l + (1+\beta)mn_v v_v. \quad \dots (6)$$

We may also write

$$r = v_l/v_v, \quad \dots (7)$$

where r is the ratio of the velocity of the molecules escaping from the liquid to that of those in the vapour space.

We therefore have for the reaction in excess of the atmospheric pressure at any moment

$$R = mLv_l - mn_v v_v \{ \beta(r+1) - (r-1) \}, \quad \dots (8)$$

$$\text{or} \quad R = mLv_l - \frac{\Pi(r+1)}{2} \left\{ \beta - \frac{r-1}{r+1} \right\} \quad \dots (9)$$

If we deal with area A the mass of the discharge per second, D , may be written

$$D = mL A, \quad \dots (10)$$

whence the total reaction is given by

$$R = Dv_l + \frac{\Pi A}{2}(r-1) - \frac{\Pi A}{2}(r+1)\beta. \quad \dots (11)$$

Note.—For the particular case in which the liquid and vapour are at the same temperature we have $v_l = v_v$ and $r = 1$. Writing $r = 1$ in (11) we have

$$R = Dv_l - \beta \Pi A, \quad . \quad . \quad . \quad . \quad . \quad (12)$$

or from equation (8)

$$R = mv_v A \{L - 2\beta n_v\}. \quad . \quad . \quad . \quad . \quad (13)$$

If, as on page 647 of the Argument, we suppose $\beta = 1$ when $r = 1$ (a condition unattainable in practice but nevertheless of interest in what follows), we should have $R = 0$ until L exceeded $2n_v$, i. e. until twice as many molecules were emitted as would have been incident upon the surface if there had been no interference. This is equivalent to writing $Dv_l = \Pi A$. For $\Pi = 10^6$ dynes, unit area, and $v_l = 6.6 \times 10^4$ cms. per second for steam at 100°C. , the maximum value of D attainable theoretically without a reaction is given by $D = 10^6 / 6.6 \times 10^4 = 15$ gms. approximately.

SECTION 9.

Theoretical investigation relating to the efflux of vapour molecules from a boiler under steady conditions.

The equations arrived at from the consideration of the conditions under which a liquid evaporates (Section 8) are without modification applicable to the discharge of vapour from an orifice. For steam escaping from an aperture in the vertical side of a boiler, as in the apparatus shown in fig. 1, we see that the case is simpler, because there is no need to take account of the weight of the apparatus, also as there can be no reflexion at the aperture of molecules advancing towards it from outside, we have $\alpha = 0$ as before. R is now measured by the torsion of the wire, and we have equation (11) holding good, namely

$$R = Dv_l + \frac{\Pi A}{2} (r - 1) - \frac{\Pi A}{2} (r + 1)\beta, \quad . \quad . \quad (11)$$

where v_l now applies to the molecules leaving the "effective aperture."

SECTION 10.

Previous experiments bearing upon an evaporative reaction.

Osborne Reynolds has described an experiment in which two pith balls were suspended at the ends of a light beam by a torsion fibre within a vessel containing water-vapour under reduced pressures. It was found that at pressures below about 2.5 mm., a flame held outside the vessel appeared to repel the nearest pith ball and a lump of ice to attract it. Reynolds * explains the phenomenon in these terms :—

“According to the kinetic theory, the molecules which constitute the gas are in rapid motion, and the pressure which the gas exerts against the bounding surface is due to the successive impulses of these molecules, whose course directs them against the surface, from which they rebound with unimpaired velocity. According to this theory, therefore, whenever a molecule of liquid leaves the surface henceforth to become a molecule of gas, it must leave it with a velocity equal to that with which the other particles of gas rebound, that is to say, instead of being just detached and quietly passing off into the gas, it must shoot off with a velocity greater than that of a cannon ball. Whatever may be the nature of the forces which give it the velocity, and which consume the latent heat in doing so, it is certain, from the principle of the conservation of momentum, that they must react on the surface with a force equal to that exerted on the molecule, just as in a gun the pressure of the powder on the breech is the same as on the shot.

“The impulse on the surface from each molecule which is driven off by evaporation must therefore be equal to that caused by the rebound of one of the reflected molecules, supposing all the molecules to be of the same size; that is to say, since the force of rebound will be equal to that of stopping, the impulse from a particle driven off by evaporation will be half the impulse received from the stopping and reflection of a particle of gas at the surface. Thus the effect of evaporation will be to increase the number of impulses on the surface; and although each of the new impulses will only be half as effective as the ordinary ones, they will add to the pressure.”

This is a delightfully clear picture of the molecular motions near an evaporating surface, but it does not take into account the interference between the opposing streams of molecules, which we have shown to be a vital part of the phenomenon of molecular discharges.

* O. Reynolds, Roy. Soc. Proc. A. p. 401 (1874).

LXVI. *The Whirling of an Overhung Eccentrically Loaded Shaft.* By S. LEES, M.A., St. John's College, Cambridge*.

Introduction.

§ 1. IN the Phil. Mag. vol. xxxvii. p. 515 (1919), the author contributed a paper under the above title, dealing with the problem of a whirling overhung shaft of negligible weight provided at its unsupported end with a disk flywheel which is not perfectly balanced. The formula for the whirling speed given in equation (18) of the paper agrees with the result obtained by Chree †, whilst the steady motion given by equation (17) of the paper is new, so far as the author knows. Unfortunately, some serious errors arise in the paper, and the periods obtained are wrong. In addition, the author's results indicated that when the whirling speed was exceeded, the shaft became unstable. This is contrary to the results of observation. The author is indebted to Prof. W. McF. Orr, F.R.S., not only for pointing out these errors, but for giving him valuable criticisms as to the method of attack adopted in the paper referred to. These criticisms have led to the following paper, in which the whole of the questions involved are dealt with, and in addition, some new points of view are given.

In connexion with the previous paper (*loc. cit.*) by the author on this subject, it was at first objected to by Prof. Orr that the use of Lagrange's equations in obtaining the results there found was not legitimate. It would now appear that the chief objection to the author's development lay not in such use of the Lagrangian method, which is here quite legitimate, but in the choice of coordinates. These were not sufficiently general to define the dynamical system under all circumstances. Thus (and the same error was made by Chree) the author assumed that the shaft could be treated as if its geometrical axis were constrained to rotate round the axis of bearings. The present paper endeavours to show that whilst this is no doubt true for steady motion, it is not true in general. Thus the present paper verifies Chree's result for the whirling speed and the author's result for the steady bending for any given speed, but for the periods gives quite different results from those obtained previously by the author. It would appear that the problem really discussed in this previous paper by the author was that of the whirling of a shaft compelled to remain in one diametral plane, which plane is itself compelled to rotate with the shaft at the constrained end.

* Communicated by the Author.

† Phil. Mag., May 1904.

Neglect of Torsional Effects.

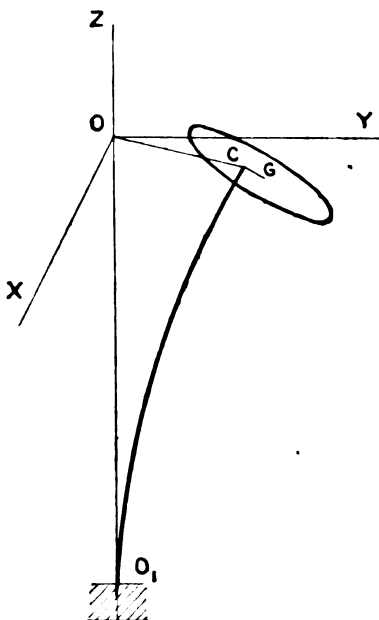
§ 2. In the paper referred to and in what follows the assumption is made that the whirling load can be taken as a perfectly true disk flywheel mounted slightly eccentrically on the shaft. It is also assumed that torsional effects are negligible. This last proviso requires a slight discussion.

It is clear that for negligible twisting of the shaft, we must have (1) the eccentricity of the load, i. e., the displacement of the centre of gravity of the flywheel from the axis of the shaft when at rest, small compared with the radius of gyration K of the flywheel about the axis of the shaft; (2) the time of a torsional oscillation small compared with the time of an oscillation involving pure bending only. A discussion of these two times of oscillation shows that the length L of the shaft from the bearing of the flywheel must be large compared with K . Throughout the present paper, this will be assumed, and torsional effects will be neglected.

Coordinates specifying the Configuration.

§ 3. To specify the position of the shaft, we shall employ four coordinates. Referring to fig. 1, we shall take it that

Fig. 1.



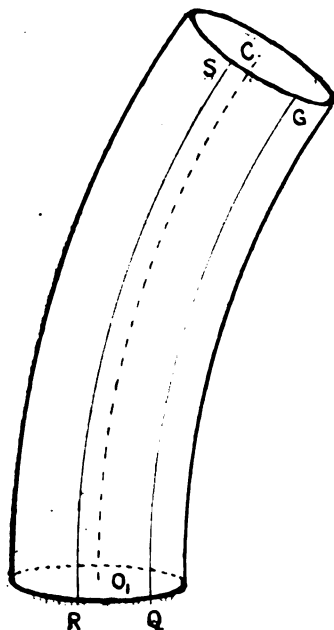
the deflexions of the shaft from the straight original condition are small, and that the movement of the free end of the

axis parallel to the direction of the axis at the constrained end is absolutely negligible. The free end C of the axis may therefore be considered to move in a plane perpendicular to the axis of bearings. The axes of reference will accordingly be taken such that the constrained axis coincides with Oz , whilst Ox and Oy lie in the plane just referred to. The coordinates of C will thus be $(x, y, 0)$. In addition, we shall require the direction-cosines of the tangent to the axis at its free end. These will be taken as $(\lambda, \mu, 1)$. The four coordinates specifying the position of the shaft are thus x, y, λ, μ .

We have yet to define the position of the centre of gravity G of the flywheel. The distance CG (the eccentricity of the flywheel) will be denoted by b . It may easily be shown that, provided torsional effects may be neglected, the angular motion of the line CG is the same as that of the shaft at its constrained end. This result, which is purely kinematical, arises as follows:—

Assume that the shaft is of radius b , so that G lies on its outer surface (see fig. 2). By taking the generator on the

Fig. 2.



surface of the shaft which passes through G, we obtain, corresponding to G, a point Q on the cross-section of the

shaft at the constrained end O_1 . If we take on this cross-section a point R, so that O_1R is parallel to the plane xOx , we can find the corresponding point S on the cross-section at the free end lying on the generator through R. If O_1 represent the centre of the shaft at the constrained end, we must have in all cases angle $RO_1Q = \text{angle } SCG$. If the shaft be compelled to turn uniformly with angular velocity ω at the constrained end (by means of a heavy flywheel at the constrained end), then the angle SCG must increase at the constant rate ω . Now the relationship between S and R is one purely depending on the *shape* of the bent shaft. If, then, we consider the purely geometrical relationship involved in the most general type of small bending deformation* of the shaft (*i. e.*, not necessarily assuming that the axis of the shaft lies in one plane), we see that to the degree of approximation here taken, the projection (on the plane RO_1Q) of SC is always parallel to RO_1 , and, in consequence, CG rotates in the plane xOy with uniform angular velocity ω . This result is clearly independent of the assumption that the shaft is of radius b .

We are thus entitled to take as the coordinates of G the values

$$x_G = x + b \cos(\omega t + \alpha), \quad y_G = y + b \sin(\omega t + \alpha), \quad z_G = 0. \quad (1)$$

Here α represents the angle which CG makes with Ox when $t=0$.

Equations of Motion.

§ 4. In order to get the equations of motion involving λ and μ , we make use of the following theorem: If a rigid body have moments of inertia A, B, C (with $B=A$) about mutually perpendicular principal axes OA, OB, OC respectively, where O is fixed relatively to the body and is either fixed in space or, if in motion, coincides with the centre of gravity, and if the angular velocities ω_1, ω_2 about the principal axes OA, OB respectively be always small compared with ω_3 , the angular velocity about OC, then correct to the first order of small quantities:—

Moment of momentum about

$$Ox = C\lambda\omega_3 - A\dot{\mu}, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and about

$$Oy = C\mu\omega_3 + A\dot{\lambda}. \quad . \quad . \quad . \quad . \quad (3)$$

* A deformation due to pure bending might be defined as one in which the projection of any straight line in the cross-section of the shaft on a plane normal to the fixed end of the axis remains parallel to its original direction.

Here the axes OX, OY, and OZ (mutually perpendicular) are fixed, and OZ is such that OC nearly coincides with it; also λ , μ , ν are the direction-cosines of OC referred to O*x*, O*y*, O*z* respectively, so that λ and μ are small, and ν may be taken as unity.

To prove this theorem, we note that

$$\omega_x = \omega_1 \cos AOX + \omega_2 \cos BOX + \omega_3 \cos COX,$$

and hence moment of momentum about

$$\begin{aligned} OX &= A(\omega_1 \cos AOX + \omega_2 \cos BOX) + C\omega_3 \cos COX \\ &= A(\omega_x - \lambda\omega_3) + C\lambda\omega_3. \quad \dots \dots \dots (4) \end{aligned}$$

Now the point (λ , μ , ν) lies on OC at unit distance from O; hence such point has velocities

$$\dot{\lambda} = \nu\omega_y - \mu\omega_z, \quad \dot{\mu} = \lambda\omega_z - \nu\omega_x, \quad \dot{\nu} = \mu\omega_x - \lambda\omega_y,$$

and it follows that

$$\begin{aligned} \mu\dot{\nu} - \nu\dot{\mu} &= \omega_x(\mu^2 + \nu^2) - \lambda\mu\omega_y - \nu\lambda\omega_z \\ &= \omega_x - \lambda(\lambda\omega_x + \mu\omega_y + \nu\omega_z) = \omega_x - \lambda\omega_3. \end{aligned}$$

Under our assumptions ν is constant at the value unity; hence (4) may be written $-A\dot{\mu} + C\lambda\omega_3$, which agrees with (2). The expression (3) is similarly obtained.

To get the forces acting on the shaft due to independent bendings in two perpendicular planes, twisting being neglected, we take for the potential energy

$$V = 2EA_1k^2\{3(x^2 + y^2) - 3L(\lambda x + \mu y) + L^2(\lambda^2 + \mu^2)\}/L^3. \quad (5)$$

This may be regarded as a generalization of the result given by Rayleigh ('Sound,' vol. i. § 183). The notation is such that E represents Young's Modulus for the material of the shaft, A_1 represents the area of cross-section which has a radius of gyration k about any diameter, whilst L is the length of the shaft from the bearing to the free end. For convenience, we shall write $B_1 = 2EA_1k^2/L^3$.

From (5), the restoring force parallel to O*x* is

$$\frac{\partial V}{\partial x} = 3B_1(2x - L\lambda), \quad \dots \dots \dots (6)$$

whilst the restoring couple parallel to the plane zOx is

$$\frac{\partial V}{\partial \lambda} = B_1(-3Lx + 2L^2\lambda). \quad \dots \dots \dots (7)$$

Similar results hold for the restoring force parallel to O*y*, and for the restoring couple parallel to the plane zOy .

The equations of motion of the system of shaft and eccentrically loaded flywheel are now obtained in the form

$$\frac{d^2}{dt^2} [x + b \cos (\omega t + \alpha)] + 3B_1(2x - L\lambda)/M = 0, \quad (8)$$

$$\frac{d^2}{dt^2} [y + b \sin (\omega t + \alpha)] + 3B_1(2y - L\mu)/M = 0, \quad (9)$$

$$\frac{d}{dt} (C\lambda\omega - A\dot{\mu}) - B_1(-3Ly + 2L^2\mu) = 0, \quad (10)$$

$$\frac{d}{dt} (C\mu\omega + A\dot{\lambda}) + B_1(-3Lx + 2L^2\lambda) = 0. \quad (11)$$

In the equations (8) and (9) M stands for the mass of the eccentrically loaded flywheel; whilst in (10) and (11) the moments of the restoring forces round the axes through G are neglected (being of the second order).

Solution of the Equations of Motion.

§ 5. The effect of the terms in $\frac{\cos}{\sin} (\omega t + \alpha)$ in the above equations is clearly that of a disturbing force. To find the "free" oscillations, we have to solve

$$(D^2 + 6B_1/M)x - 3B_1L\lambda/M = 0, \quad (12)$$

$$(D^2 + 6B_1/M)y - 3B_1L\mu/M = 0, \quad (13)$$

$$-3B_1Lx + (AD^2 + 2B_1L^2)\lambda + C\omega D\mu = 0, \quad (14)$$

$$-3B_1Ly + (AD^2 + 2B_1L^2)\mu - C\omega D\lambda = 0. \quad (15)$$

In these equations D denotes d/dt . To solve them, we write

$$x = r \cos (pt + \gamma), \quad y = r \sin (pt + \gamma), \quad \lambda = \theta \cos (pt + \gamma), \\ \mu = \theta \sin (pt + \gamma). \quad (16)$$

Here r and θ are constants which are connected, however, so that only one of them is arbitrary. To determine r/θ and p , we have

$$(-p^2 + 6B_1/M)r - 3B_1L\theta/M = 0, \quad (17)$$

$$-3B_1Lr + (-Ap^2 + 2B_1L^2 + C\omega p)\theta = 0. \quad (18)$$

Elimination of r and θ between (17) and (18) gives for the periods

$$\begin{vmatrix} -p^2 + 6B_1/M, & -3B_1L/M, \\ -3B_1L, & -Ap^2 + C\omega p + 2B_1L^2, \end{vmatrix} = 0. \quad (19)$$

It may be remarked that the bi-quadratic equation (19) has four real roots, as is easily seen on noticing the change of sign of the expression on the left-hand side, when for p is substituted in succession the values $-\infty$, $-\sqrt{6B_1/M}$, 0 , $\sqrt{6B_1/M}$, ∞ . For any one of the four periods, the corresponding ratio of r to θ is given by either (18) or (19).

The most general "free" motion is a linear combination of expressions of the type (16) corresponding to the four periods. To each motion of the type (16), there are two arbitrary constants, viz., r and γ . Hence, the general solution involves eight arbitrary constants, which is clearly correct to enable arbitrarily assigned values to be given to x , $\dot{x}$, y , $\dot{y}$, λ , $\dot{\lambda}$, μ , and $\dot{\mu}$. The existence of four real periods p implies that so far as the "free" or "natural" vibrations are concerned, there is no question of instability.

To complete the solution of equations (8) to (11), we require the "forced" oscillation due to the terms in $\frac{\cos}{\sin}(\omega t + \alpha)$, i. e. due to want of balance in the flywheel. Such an oscillation is obtained by supposing the centre of the flywheel or disk to describe a circle of radius R with angular velocity ω in the same direction as the rotation of the shaft. Such a motion must satisfy

$$x = R \cos(\omega t + \alpha), \quad y = R \sin(\omega t + \alpha), \text{ etc.,}$$

and thus

$$(6B_1/M - \omega^2)R - 3B_1L\Theta/M = \omega^2b,$$

$$-3B_1LR + (2L^2B_1 - A\omega^2 + C\omega^2)\Theta = 0;$$

where Θ represents the steady deviation of the free end of the shaft in such a motion. From these equations we find

$$\frac{R}{2L^2B_1 - A\omega^2 + C\omega^2} = \frac{\Theta}{3BL} = \frac{\omega^2 b}{(6B_1/M - \omega^2)(2L^2B_1 - A\omega^2 + C\omega^2) - 9B_1^2L^2/M}. \quad (20)$$

This agrees with the result (equation 17) given in the author's previous paper (*loc. cit.*) Whirling will take place when

$$(6B_1/M - \omega^2)(2L^2B_1 - A\omega^2 + C\omega^2) - 9B_1^2L^2/M = 0, \quad (21)$$

for in this case the values of R and Θ become infinite. It may be noted that (21) agrees with Chree's result (see *Phil. Mag.*, May 1904, equation (10)). These results accordingly indicate that whirling is the only cause of instability, and provided the internal friction of the shaft prevents the shaft from excessive whirling as the system is speeded up through

the whirling speed, once this speed is left behind, the shaft is as safe as ever. It ought to be mentioned that equation (21), which is a quadratic in ω^2 , has only one positive root for ω^2 *, so that there is only one whirling speed.

The general solution of equations (8) to (11) is obtained by combining the most general set of free oscillations with the forced circular motion given by (20). In actual practice there will be a certain amount of energy dissipation taking place, and this may be relied on to cause the terms representing the free vibrations ultimately to disappear, leaving the forced motion given by (20) representing the steady state of motion ultimately set up.

It may be noticed that in both the forced motion and in any one of the free motions typified by (16), the path of the centre of gravity G of the flywheel or disk is a circle concentric with the axis of z , i. e., the constrained axis. The axis of the shaft is also bent in one plane, which must pass through Oz and include the centre of gravity G. These results would not hold, however, for the most general motion involving all the four periods.

It is easy to verify that for speeds below the whirling speed, the centre of gravity G in the steady motion is always on the opposite side of the bent shaft to the axis Oz. For speeds above the whirling speed, G is on the same side of the bent shaft as Oz, in the steady motion.

Effect of Internal Viscosity Terms on the Motion.

§ 6. The causes of the various frictional resistances which affect the system will be complex (sound-waves, wind-resistance, viscosity of material of shaft). We shall first assume that at the constrained end of the shaft, arrangements are provided to keep the speed from falling, and for the rest, that friction is effectively represented by linear terms in the rates of variation (relative to the constrained end of the shaft) of the coordinates specifying the configuration of the system. We also assume that the frictional terms will be unaltered if the shaft be considered at rest at the bearing, and the same relative motions take place in the system; this in effect assumes that internal viscosity is the principal factor in the frictional terms.

If we take axes $O_1\xi$, $O_1\eta$ rotating with the shaft at angular velocity ω in a plane parallel to xOy , the new origin O_1 being on the axis of the shaft at its constrained end (the bearing), we may easily express the above assumptions.

* Provided, of course, the shaft is long enough, i. e. $L > 3(C - A)/M$.

Relative to such axes, we have to change the constant B_1 to $B_1(1 + \alpha D/Dt)$, where D/Dt represents differentiation with the moving axes. The constant α is a constant of viscosity.

The restoring force parallel to $O_1\xi$ instead of being $3B_1(2\xi - Ll)$ is now $3B_1(1 + \alpha D/Dt)(2\xi - Ll)$. The direction-cosines of the end of the shaft at C relative to the moving axes and the axis of z are now taken as $l, m, 1$. Thus the viscous force Ξ in the direction $O_1\xi$ is

$$3B_1\alpha \frac{D}{Dt} (2\xi - Ll).$$

Similarly, parallel to $O_1\eta$, we get the viscous force

$$H = 3B_1\alpha \frac{D}{Dt} (2\eta - Lm).$$

Now the viscous force along the *fixed* axis Ox is

$$X = \Xi \cos \omega t - H \sin \omega t, \quad \dots \quad (22)$$

whilst

$$\xi = x \cos \omega t + y \sin \omega t$$

and

$$\eta = -x \sin \omega t + y \cos \omega t.$$

On evaluating (22), and employing

$$l = \lambda \cos \omega t + \mu \sin \omega t,$$

$$m = -\lambda \sin \omega t + \mu \cos \omega t,$$

we find that

$$X = 6B_1\alpha(\dot{x} + \omega y)/M - 3B_1L\alpha(\dot{\lambda} + \omega\mu)/M. \quad \dots \quad (23)$$

By similar reasoning, the viscous force parallel to the fixed axis Oy is

$$Y = 6B_1\alpha(\dot{y} - \omega x)/M - 3B_1L\alpha(\dot{\mu} - \omega\lambda)/M. \quad \dots \quad (24)$$

A similar procedure to the above gives the viscous couples, and we are led to the equations of motion

$$\left. \begin{aligned} (D^2 + 6B_1/M)x - 3B_1L\lambda/M + 6B_1\alpha(\dot{x} + \omega y)/M \\ \quad - 3B_1L\alpha(\dot{\lambda} + \omega\mu)/M = b\omega^2 \cos \omega t, \\ (D^2 + 6B_1/M)y - 3B_1L\mu/M + 6B_1\alpha(\dot{y} - \omega x)/M \\ \quad - 3B_1L\alpha(\dot{\mu} - \omega\lambda)/M = b\omega^2 \sin \omega t, \\ -3B_1Lx + (AD^2 + 2B_1L^2)\lambda + C\omega D\mu \\ \quad - 3B_1\alpha L(\dot{x} + \omega y) + 2B_1\alpha L^2(\dot{\lambda} + \omega\mu) = 0, \\ -3B_1Ly + (AD^2 + 2B_1L^2)\mu - C\omega D\lambda \\ \quad - 3B_1\alpha L(\dot{y} - \omega x) + 2B_1\alpha L^2(\dot{\mu} - \omega\lambda) = 0, \end{aligned} \right\}. \quad (25)$$

where, as before, D stands for d/dt .

These equations can be solved in the usual way, when it will be seen that the effect of internal viscous effects is to modify slightly the periods given by (19) and to introduce damping. It is easy to see, however, that the forced motion is not affected in the slightest, as terms of the type $(\dot{x} + \omega y)$ then disappear. Hence for whirling, (21) still holds.

For a perfectly balanced shaft we may put $b=0$. In such a case, it may appear at first sight that there is a possibility of there being a state of steady motion with x , y , λ , and μ constant. That there is no such possibility may be seen by first wiping out all terms in equations (25) involving d/dt , and thence showing that the eliminant of the simple linear equations left can never vanish*.

Friction which may prevent Whirling.

§ 7. Although purely internal elastic (or viscous) friction does not in the slightest degree prevent whirling, yet external friction (*e. g.*, of air) of a suitable type may do so. We shall consider the case of such external frictional effects being dependent linearly on the coordinate velocities, which have no longer to be referred to moving axes. A simple case would be obtained by changing B_1 into $B_1(1 + \beta d/dt)$, where d/dt has now no reference to moving axes. A more general case could be obtained by assuming a dissipation function

$$F = \frac{1}{2}(K_1\dot{x}^2 + 2K_2\dot{x}\lambda + K_3\dot{\lambda}^2 + K_4\dot{y}^2 + 2K_5\dot{y}\mu + K_6\dot{\mu}^2), \quad (26)$$

such that, *e. g.*, the frictional force parallel to Ox is $\partial F/\partial \dot{x}$, the frictional couple in the plane zOx is $\partial F/\partial \dot{\lambda}$. Without going into the details, it will be noticed that the effect of friction in these cases will be (1) to alter the period equations slightly and thus to give rise to damping of the free vibrations; (2) to prevent the forced oscillation from ever becoming infinite. The general argument for the latter statement will be found in Rayleigh's 'Sound,' vol. i. § 104. Thus friction of the type indicated may enable the system to pass through the critical speed, without disaster occurring.

Elastic Yielding at the Bearing.

§ 8. The effect of elastic yielding at the bearing will now be discussed with the assumption that the forces involved are not sufficient to produce any appreciable movement at the

- * The vanishing of the eliminant would require

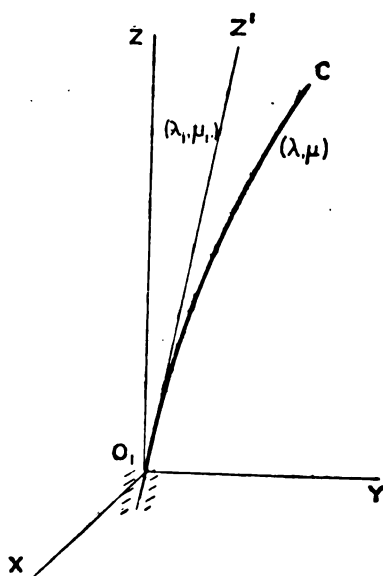
$$17\omega^4\alpha^4 + 2\omega^2\alpha^2 + 1 = 0,$$

which for real values of ω can never be satisfied.

centre of the bearing, but only produce small changes in the direction of the *axis* of the bearing. For the sake of generality, this yielding will be taken as different (for the same bending moment) for two directions at right angles to one another.

Referring to fig. 3, let the direction-cosines of the deflected axis of the bearing at O_1 relative to fixed axes be $\lambda_1, \mu_1, 1$, and of the axis of the shaft at C be $\lambda, \mu, 1$. Relative to $O_1 z'$ *,

Fig. 3.



the direction-cosines are $\lambda_2 (= \lambda - \lambda_1)$, $\mu_2 (= \mu - \mu_1)$, 1, correct to first order terms. If x and y be the coordinates of the centre of the shaft at C relative to the same fixed axes, then relative to $O_1 z'$, the coordinates are

$$x_2 = x - L\lambda_1, \quad y_2 = y - L\mu_1.$$

The energy of bending of the shaft is

$$B_1 \{ 3(x_2^2 + y_2^2) - 3L(\lambda_2 y_2 + \mu_2 y_2) + L^2(\lambda_2^2 + \mu_2^2) \}. \quad (27)$$

We shall take the energy of deformation of the bearing as

$$\frac{1}{2}(P\lambda_1^2 + Q\mu_1^2), \quad \dots \dots \dots (28)$$

where the constant P is not assumed to be equal to Q , and a term involving $\lambda_1 \mu_1$ is omitted. The bending moment at O_1 in a plane parallel to zO_1x is accordingly $d(\frac{1}{2}P\lambda_1^2)/d\lambda_1 = P\lambda_1$.

* The other axes may here be taken as lying in the planes zO_1x , zO_1y .

Similarly, we get $Q\mu_1$ for the bending moment in a plane parallel to zO_1y . The restoring force at C parallel to O_1x is $3B_1(2x_2 - L\lambda_2)$, whilst the bending moment at C in the same plane zO_1x is $B_1(-3Lx_2 + 2L^2\lambda_2)$. Hence the bending moment at O_1 in the same plane (zO_1x) is also

$3B_1(2x_2 - L\lambda_2)L + B_1(-3Lx_2 + 2L^2\lambda_2) = 3B_1Lx_2 - B_1L^2\lambda_2$,
which must equal $P\lambda_1$. Hence

$$P\lambda_1 = 3B_1L(x - L\lambda_1) - B_1L^2(\lambda - \lambda_1),$$

or $\lambda_1 = (3B_1Lx - B_1L^2\lambda)/(P + 2B_1L^2), \quad \dots \quad (29)$

Similarly $\mu_1 = (3B_1Ly - B_1L^2\mu)/(Q + 2B_1L^2). \quad \dots \quad (30)$

Thus the total potential energy is

$$\begin{aligned} V = B_1 \{ & 3[(x - L\lambda_1)^2 + (y - L\mu_1)^2] - 3L[(\lambda - \lambda_1)(x - L\lambda_1) \\ & + (\mu - \mu_1)(y - L\mu_1)] + L^2[(\lambda - \lambda_1)^2 \\ & + (\mu - \mu_1)^2] \} + \frac{1}{2}P\lambda_1^2 + \frac{1}{2}Q\mu_1^2, \quad \dots \quad (31) \end{aligned}$$

where λ_1 and μ_1 are to be replaced by their values (29) and (30) respectively.

If we write $B_1L^2/(P + 2B_1L^2) = \alpha,$

and $B_1L^2/(Q + 2B_1L^2) = \beta,$

where α and β need not necessarily be small, we find for example :

Restoring force parallel to Ox

$$= 3B_1 \left[2x \left(1 - \frac{3\alpha}{2} \right) - L\lambda(1 - \alpha) \right]. \quad \dots \quad (32)$$

Restoring couple in plane zO_1x

$$= B_1 \left[-3Lx(1 - \alpha) + 2L^2\lambda \left(1 - \frac{\alpha}{2} \right) \right]. \quad \dots \quad (33)$$

The equations of motion of the system now become (neglecting frictional effects)

$$\left. \begin{aligned} \frac{d^2}{dt^2} (x + b \cos \omega t) + 3B_1 \left[2x \left(1 - \frac{3\alpha}{2} \right) - L\lambda(1 - \alpha) \right] / M &= 0, \\ \frac{d^2}{dt^2} (y + b \sin \omega t) + 3B_1 \left[2y \left(1 - \frac{3\beta}{2} \right) - L\mu(1 - \beta) \right] / M &= 0, \\ \frac{d}{dt} (C\lambda\omega - A\dot{\mu}) - B_1 \left[-3Ly(1 - \beta) + 2L^2\mu \left(1 - \frac{\beta}{2} \right) \right] &= 0, \\ \frac{d}{dt} (C\mu\omega + A\dot{\lambda}) + B_1 \left[-3Lx(1 - \alpha) + 2L^2\lambda \left(1 - \frac{\alpha}{2} \right) \right] &= 0. \end{aligned} \right\} \quad (34)$$

For the natural periods (ignoring the terms in b), we find solutions of the type

$$\left. \begin{aligned} x &= r_1 \cos (pt + \gamma), & \lambda &= \theta_1 \cos (pt + \gamma), \\ y &= r_2 \sin (pt + \gamma), & \mu &= \theta_2 \sin (pt + \gamma). \end{aligned} \right\} \quad (35)$$

Of the four constants ($r_1, r_2, \theta_1, \theta_2$) only one is arbitrary, the others being given by (34). For the values of p , we have the equation

$$\Delta(p) =$$

$$\left| \begin{array}{cccc} -p^2 + \frac{6B_1}{M} \left(1 - \frac{3\alpha}{2}\right), & 0, & \frac{-3B_1L}{M} (1 - \alpha), & 0 \\ 0, & -p^2 + \frac{6B_1}{M} \left(1 - \frac{3\beta}{2}\right), & 0, & \frac{-3B_1L}{M} (1 - \beta) \\ 0, & 3B_1L(1 - \beta), & -C\omega p, & Ap^2 - 2B_1L^2 \left(1 - \frac{\beta}{2}\right) \\ 3B_1L(1 - \alpha), & 0, & Ap^2 - 2B_1L^2 \left(1 - \frac{\alpha}{2}\right), & -C\omega p \end{array} \right| = 0. \quad (36)$$

This is a bi-quadratic in p^2 , and for small values of α and β , the values of p will differ little from those given by (19). We may take it that the natural oscillations will ultimately be damped out. The steady forced oscillation left can be obtained by assuming

$$\left. \begin{aligned} x &= R_1 \cos \omega t, & \lambda &= \Theta_1 \cos \omega t, \\ y &= R_2 \sin \omega t, & \mu &= \Theta_2 \sin \omega t. \end{aligned} \right\} \quad (37)$$

Substituting these values in equations (34), we find

$$\left. \begin{aligned} R_1 \left\{ 6B_1 \left(1 - \frac{3\alpha}{2}\right) / M - \omega^2 \right\} - 3B_1L\Theta_1(1 - \alpha) / M &= \omega^2 b, \\ R_2 \left\{ 6B_1 \left(1 - \frac{3\beta}{2}\right) / M - \omega^2 \right\} - 3B_1L\Theta_2(1 - \beta) / M &= \omega^2 b, \\ 3B_1L(1 - \beta)R_2 - C\omega^2\Theta_1 + \Theta_2 \left\{ A\omega^2 - 2B_1L^2 \left(1 - \frac{\beta}{2}\right) \right\} &= 0, \\ 3B_1L(1 - \alpha)R_1 - C\omega^2\Theta_2 + \Theta_1 \left\{ A\omega^2 - 2B_1L^2 \left(1 - \frac{\alpha}{2}\right) \right\} &= 0. \end{aligned} \right\} \quad (38)$$

The four equations (38) determine R_1, R_2, Θ_1 , and Θ_2 . If the determinant arising out of the left-hand sides of these equations (on elimination of R_1, R_2, Θ_1 , and Θ_2) vanishes, the amplitudes R_1 , etc. become infinite, and we get whirling. The whirling equation is easily seen to be the result of substituting ω for p in the equation (36).

The path of the free extremity C of the axis of the shaft is the ellipse

$$x^2/R_1^2 + y^2/R_2^2 = 1. \quad (39)$$

This elliptical path is to be expected when the constrained end of the axis is not very rigidly held.

§ 9. We shall now discuss at greater length some of the points involved in § 8.

With regard to the period equation (36), it is possible to show that this equation always has real positive roots for p^2 , and hence (except at a whirling speed) there is no question of instability. To prove this statement, we follow the method outlined by Routh ('Rigid Dynamics, vol. ii. p. 50 (1905)).

We write (36) in the form

$\Delta =$

$$\begin{vmatrix} -p^2 + \frac{6B_1}{M}\left(1 - \frac{3\alpha}{2}\right) & 0 & -\frac{3B_1L}{M}(1-\alpha) & 0 \\ 0 & -p^2 + \frac{6B_1}{M}\left(1 - \frac{3\beta}{2}\right) & 0 & -\frac{3B_1L}{M}(1-\beta) \\ -3B_1L(1-\alpha) & 0 & -Ap^2 + 2B_1L^2\left(1 - \frac{\alpha}{2}\right) & C\omega p \\ 0 & -3B_1L(1-\beta) & C\omega p & -Ap^2 + 2B_1L^2\left(1 - \frac{\beta}{2}\right) \end{vmatrix} = 0. \quad (36 a)$$

and denote by Δ_1 the first minor obtained by deleting the first row and the first column. The second minor obtained by deleting the first row and first column of Δ_1 may be denoted by Δ_2 . We proceed similarly for Δ_3 , which will be $-Ap^2 + 2B_1L^2\left(1 - \frac{\beta}{2}\right)$. We also let $\Delta_4 = 1$. Each of the determinants referred to will be a function of p^2 , and clearly when $p^2 = \infty$, we shall have

$$\Delta = \infty, \Delta_1 = -\infty, \Delta_2 = \infty, \Delta_3 = -\infty, \Delta_4 = 1.$$

In this series, we have four changes of sign.

We now consider the values of the determinants when we take $p^2 = 0$. In this case, we find

$$\Delta = \begin{vmatrix} \frac{6B_1}{M}\left(1 - \frac{3\alpha}{2}\right) & -\frac{3B_1L}{M}(1-\alpha) \\ -3B_1L(1-\alpha) & 2B_1L^2\left(1 - \frac{\alpha}{2}\right) \end{vmatrix} \begin{vmatrix} \frac{6B_1}{M}\left(1 - \frac{3\beta}{2}\right) & -\frac{3B_1L}{M}(1-\beta) \\ -3B_1L(1-\beta) & 2B_1L^2\left(1 - \frac{\beta}{2}\right) \end{vmatrix} \quad (40)$$

Hence (assuming that α and β are both positive and less * than $\frac{1}{2}$) we get Δ positive. We also find

$$\Delta_1 = -\frac{3R_1^3 I_1^4}{M} \left(1 - \frac{\alpha}{2}\right) (1 - 2\beta), \quad . \quad . \quad (41)$$

which is also positive, provided $\beta < \frac{1}{2}$. Similarly, Δ_2 , Δ_3 , and Δ_4 are positive, and there are no changes in sign in the series Δ , Δ_1 , Δ_2 , Δ_3 , and Δ_4 . In consequence, in going from $p^2=0$ to $p^2=\infty$, four changes of sign are gained in the series Δ , Δ_1 , etc., and the roots (in p^2) of the bi-quadratic (36 a) all lie between 0 and ∞ . Hence p is always real.

We proceed to discuss the question of whirling. Solving equations (38) in the usual way for R_1 (say), we find

$$\begin{aligned} -\frac{R_1 \bar{\Delta}}{\omega^2 b} = & \left\{ \frac{6B_1}{M} \left(1 - \frac{3\beta}{2}\right) - \omega^2 \right\} \\ & \left\{ C\omega^4 - \left[A\omega^2 - 2B_1 L^2 \left(1 - \frac{\alpha}{2}\right) \right] \left[A\omega^2 - 2B_1 L^2 \left(1 - \frac{\beta}{2}\right) \right] \right\} \\ & + \frac{9B_1^2 L^2}{M} (1-\alpha)(1-\beta) C\omega^2 - \frac{9B_1^2 L^2}{M} (1-\beta)^2 \\ & \left[A\omega^2 - 2B_1 L^2 \left(1 - \frac{\alpha}{2}\right) \right], \quad . \quad . \quad (42) \end{aligned}$$

where $\bar{\Delta}$ is the determinant obtained by putting $p^2=\omega^2$ in (36 a). It may be remarked that if α and β are not equal, then $\bar{\Delta}$ is not capable of being split into factors, and (42) cannot be made simpler in form. If, however, we take $\alpha=\beta$, we find

$$\begin{aligned} -\frac{R_1 \bar{\Delta}}{\omega^2 b} = & \left\{ C\omega^2 - \left[A\omega^2 - 2B_1 L^2 \left(1 - \frac{\alpha}{2}\right) \right] \right\} \cdot \\ & \cdot \left\{ \left[\frac{6B_1}{M} \left(1 - \frac{3\alpha}{2}\right) - \omega^2 \right] \left[C\omega^2 + A\omega^2 - 2B_1 L^2 \left(1 - \frac{\alpha}{2}\right) \right] \right. \\ & \left. + \frac{9B_1^2 L^2}{M} (1-\alpha)^2 \right\}, \quad . \quad . \quad (43) \end{aligned}$$

* It is actually necessary for the complete argument to restrict both α and β to values less than $\frac{1}{2}$. The definitions of α and β in § 8 show that these restrictions are satisfied.

whilst

$$\Delta = - \left\{ \left[\frac{6B_1}{M} \left(1 - \frac{3\alpha}{2} \right) - \omega^2 \right] \left[C\omega^2 - A\omega^2 + 2B_1L^2 \left(1 - \frac{\alpha}{2} \right) \right] - \frac{9B_1^2L^2}{M} (1-\alpha)^2 \right\} \\ \cdot \left\{ \left[\frac{6B_1}{M} \left(1 - \frac{3\alpha}{2} \right) - \omega^2 \right] \left[C\omega^2 + A\omega^2 - 2B_1L^2 \left(1 - \frac{\alpha}{2} \right) \right] + \frac{9B_1^2L^2}{M} (1-\alpha)^2 \right\} . \quad . \quad . \quad (44)$$

Thus the second line factor of (44) disappears in the expression for R_1 , and we get a result agreeing with (20) when $\alpha = 0$.

If α and β are not equal, we cannot get rid of a factor in this way, and whirling may occur whenever $\Delta = 0$. If we denote the minors obtained by deleting from $\bar{\Delta}$ the first row and column, first two rows and columns, etc. by $\Delta_1, \bar{\Delta}_2$, etc., exactly as above, we find when $\omega^2 = \alpha$, that (since $C > A$)

$$\bar{\Delta} = -\infty, \quad \bar{\Delta}_1 = +\infty, \quad \Delta_2 = -\infty, \quad \Delta_3 = -\infty, \quad \bar{\Delta}_4 = 1.$$

When we put $\omega^2 = 0$, we find

$$\bar{\Delta} = \begin{vmatrix} \frac{6B_1}{M} \left(1 - \frac{3\alpha}{2} \right), & \frac{3B_1L}{M} (1-\alpha) \\ 3B_1L(1-\alpha), & 2B_1L^2 \left(1 - \frac{\alpha}{2} \right) \end{vmatrix} \begin{vmatrix} \frac{6B_1}{M} \left(1 - \frac{3\beta}{2} \right), & \frac{3B_1L}{M} (1-\beta) \\ 3B_1L(1-\beta), & 2B_1L^2 \left(1 - \frac{\beta}{2} \right) \end{vmatrix}, \quad . \quad . \quad . \quad (45)$$

and is accordingly positive. We also find

$$\bar{\Delta}_1 = \frac{3B_1^3L^4}{M} \left(1 - \frac{\alpha}{2} \right) (1-2\beta), \quad . \quad . \quad (46)$$

and is thus positive. Clearly also Δ_2 is positive, whilst $\bar{\Delta}_3$ is positive and Δ_4 is unity. Thus in going from $\omega^2 = 0$ to $\omega^2 = \infty$, we gain three* changes of sign, and there are

* There are *at least* three whirling speeds, but the argument really shows that there may be three, five, or any odd number (>3) whirling speeds. The biquadratic in ω^2 (viz., $\Delta=0$) can, however, only have four roots; hence we settle once and for all that there are three positive roots only for ω^2 , and hence three real whirling speeds.

For this important point I am indebted to Prof. Orr, who observes that Routh's argument ('Rigid Dynamics,' *loc. cit.*) depends upon n variations of sign being lost or gained between $p^2 = -\infty$ and $p^2 = +\infty$, for a determinant of the n th order which equated to zero gives an equation of the n th degree in p^2 . If (as in our $\bar{\Delta}=0$), n variations of sign are *not* lost or gained (*i. e.* in our case $n=4$) between $p^2 = -\infty$ and $p^2 = +\infty$ (in our whirling equation $\bar{\Delta}=0$, p^2 is ω^2), Routh's argument must be modified in some such way as is indicated at the beginning of this footnote.

accordingly three real positive roots for ω^2 , and hence *three* whirling speeds. With a *circular* motion of the point C, however, there is only one whirling speed, because (as has already been pointed out) for $\alpha=\beta$, the numerator in the expression for R_1 vanishes for two of the speeds just given by the general theory. The two speeds referred to will be given by

$$\left[\frac{6B_1}{M} \left(1 - \frac{3x}{2} \right) - \omega^2 \right] \left[C\omega^2 + A\omega^2 - 2B_1L^2 \left(1 - \frac{\alpha}{2} \right) \right] + \frac{9B_1^2L^2}{M} (1-\alpha)^2 = 0 \quad (47)$$

If we take $\alpha=0$, we get

$$\omega^2 = B_1 \left(\frac{L^2}{C+A} + \frac{3}{M} \right) \pm B_1 \sqrt{\left(\frac{L^2}{C+A} + \frac{3}{M} \right)^2 - \frac{3L^2}{M(C+A)}}, \quad (48)$$

and these will give close approximations to the new critical speeds involved when the shaft is fairly rigidly held.

As a numerical example, we may take $C=2A$, $L^2=15A/M$. We then find the whirling speed given by (21) is obtained from $\omega^2 = (\sqrt{189}-12)B_1/M$. The two whirling speeds introduced by the imperfect rigidity of the bearing would approximately be given by $\omega^2 = B_1/M$ and $15B_1/M$. The tendency to whirl at these latter speeds might easily be masked by the effects of friction, however.

The Effect of Slight Initial Distortion of Shaft.

§ 10. If the axis of the shaft be not originally a perfect straight line, we may proceed as follows (the bearing is supposed to be rigid).

We still suppose that the coordinates of the point C for the free end of the shaft are (x, y) relative to fixed axes. The potential energy is, however, now to be taken as expression (5) with $x-\bar{x}$, $y-\bar{y}$, $\lambda-\bar{\lambda}$, $\mu-\bar{\mu}$, substituted respectively for x , y , λ , μ . Here $\bar{x}$, $\bar{y}$, $\bar{\lambda}$, $\bar{\mu}$, represent respectively the initial small values of x , y , λ , μ , due to the slight distortion. The initial bending need not be confined to one plane, and we may suppose

$$\left. \begin{aligned} \bar{x} &= b_1 \cos(\omega t + \alpha_1), & \bar{y} &= b_1 \sin(\omega t + \alpha_1), \\ \bar{\lambda} &= \theta_1 \cos(\omega t + \beta_1), & \bar{\mu} &= \theta_1 \sin(\omega t + \beta_1), \end{aligned} \right\}, \quad (49)$$

where b , θ_1 , α_1 , and β_1 are constants.

Phil. Mag. Ser. 6. Vol. 45. No. 268. April 1923. 2 Z

Instead of equations (8) to (11), we get

$$\left. \begin{aligned} \ddot{x} + 6B_1x/M - 3B_1L\lambda/M &= \omega^2b \cos \omega t \\ &+ 3B_1[2b_1 \cos(\omega t + \alpha_1) - L\theta_1 \cos(\omega t + \beta_1)]/M, \\ \ddot{y} + 6B_1y/M - 3B_1L\mu/M &= \omega^2b \sin \omega t \\ &+ 3B_1[2b_1 \sin(\omega t + \alpha_1) - L\theta_1 \sin(\omega t + \beta_1)]/M, \\ C\omega\dot{\lambda} - A\ddot{\mu} - B_1(-3Ly + 2L^2\mu) \\ &= B_1[-2L^2\theta_1 \sin(\omega t + \beta_1) + 3Lb_1 \sin(\omega t + \alpha_1)], \\ C\omega\dot{\mu} + A\ddot{\lambda} + B_1(-3Lx + 2L^2\lambda) \\ &= B_1[2L^2\theta_1 \cos(\omega t + \beta_1) - 3Lb_1 \cos(\omega t + \alpha_1)]. \end{aligned} \right\} \quad (50)$$

The free periods will be exactly the same as those given in § 5. The forced motion will involve, for each of the four coordinates, simple harmonic terms of the type $\cos \omega t$ and $\sin \omega t$. We may, in fact, assume

$$\left. \begin{aligned} x &= A_1 \cos \omega t + A_2 \sin \omega t, \\ y &= A_1 \sin \omega t - A_2 \cos \omega t, \\ \lambda &= A_3 \cos \omega t + A_4 \sin \omega t, \\ \mu &= A_3 \sin \omega t - A_4 \cos \omega t. \end{aligned} \right\} \quad (51)$$

If we substitute these values in either the first and third, or the second and fourth of equations (50), and equate the terms in $\cos \omega t$ and $\sin \omega t$ together for both sides of each of these equations, we get four equations for determining A_1, A_2, A_3 , and A_4 , viz.,

$$\left. \begin{aligned} A_1 \left(-\omega^2 + \frac{6B_1}{M} \right) - \frac{3B_1L}{M} A_3 \\ &= \omega^2b + \frac{3B_1}{M} (2b_1 \cos \alpha_1 - L\theta_1 \cos \beta_1), \\ A_2 \left(-\omega^2 + \frac{6B_1}{M} \right) - \frac{3B_1L}{M} A_4 \\ &= -\frac{3B_1}{M} (2b_1 \sin \alpha_1 - L\theta_1 \sin \beta_1), \\ -3B_1LA_1 + A_3(C\omega^2 - A\omega^2 + 2B_1L^2) \\ &= 2B_1L^2\theta_1 \cos \beta_1 - 3B_1Lb_1 \cos \alpha_1, \\ -3B_1LA_2 + A_4(C\omega^2 - A\omega^2 + 2B_1L^2) \\ &= -2B_1L^2\theta_1 \sin \beta_1 + 3B_1Lb_1 \sin \alpha_1. \end{aligned} \right\} \quad (52)$$

In the denominators of the expressions for each of $A_1, A_2,$

A_3 , and A_4 , will appear (since A_1 and A_3 are independent of A_2 and A_4)

$$\Delta_1 = \begin{vmatrix} -\omega^2 + \frac{6B_1}{M}, & -\frac{3B_1L}{M} \\ -3B_1L, & C\omega^2 - A\omega^2 + 2B_1L^2 \end{vmatrix} \quad \dots \quad (53)$$

Thus the condition for whirling is

$$\Delta_1 = 0, \quad \dots \quad (54)$$

which is precisely the same as equation (21). Thus whether we consider whirling as arising from the forced motion due to an eccentric load, or to the forced motion due to a slightly deformed shaft initially, the same result for the whirling speed is obtained.

It is quite clear from (51) that in the forced motion the path of C is a circle concentric with Oz, for

$$x^2 + y^2 = A_1^2 + A_2^2.$$

The points C and G, and the axis Oz need not now necessarily lie in the same plane.

Conclusion.

§ 11. In the present paper, the author has endeavoured to indicate the kinematics of the motion of the free end of the shaft assuming negligible torsional effects. The general equations of motion have then been deduced for an eccentrically loaded disk or flywheel, leading to the conclusion that whirling may be regarded as due to the amplitude of the steady forced oscillation of C round Oz becoming theoretically infinite at a certain speed. Alternatively, whirling (even for a symmetrically mounted flywheel) may be regarded as having a similar origin, on account of slight deviations of the centre line of the shaft from the straight line initially.

The author has endeavoured to show that elastic viscosity (in the shaft itself) cannot prevent whirling in the slightest degree, but that external friction may enable the system to pass safely through what would be a whirling speed without such friction.

The effect of elastic yielding at the bearing has been investigated both for symmetrical and unsymmetrical elasticity. The curious result is obtained that for unsymmetrical elasticity or elliptic motion there are three whirling speeds (neglecting friction). Apart from whirling, there is no question of instability, however. The two extra whirling

speeds are traced down to an effect which vanishes when the motion becomes circular. It is possible that external friction may mask these additional speeds of whirling.

Lastly, the author takes this opportunity of acknowledging his deep indebtedness to Prof. W. McF. Orr, for his many valuable suggestions and criticisms whilst the material of this paper has been thrashed out. But for him this paper could not have been written in anything like its present form.

LXVII *Note on Mr. Lees' Paper on the Whirling of an Overhung Shaft.* By Prof. W. McF. ORR, D.Sc., F.R.S.*

THIS note originated from a correspondence with Mr. Lees. My objection to his use of Lagrange's equation was by no means the only point about which he showed me that I was in error.

§1. *If the three moments of inertia are unequal the motion is unstable at high speeds.*

In connexion with the problem discussed by Mr. Lees it occurred to me to test for stability in case the three moments of inertia, A, B, C, of the pulley relative to its centre of mass are all unequal. There are then two "whirling" speeds, each being that for the same shaft loaded with a symmetrical pulley, having moments A, A, C in one case and B, B, C in the other. And, to my surprise, I found that the "free" motion for a perfectly centred pulley is exponentially unstable if either of these speeds is exceeded. This may explain the fact, of which I have been informed by my former colleague, Mr. H. H. Jeffcott †, that propellers (of aeroplanes) having two blades show evidence of instability.

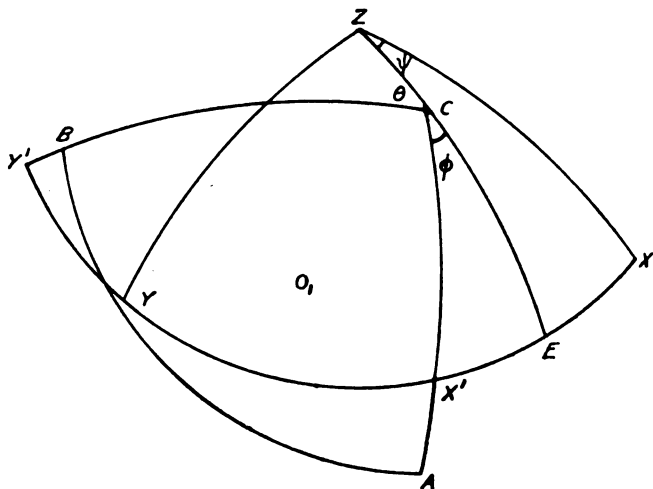
Although I solved the problem first in Lees' coordinates, apparently the shortest way of doing so is to follow Routh's treatment of the unsymmetrical top (Rigid Dynamics, 4th edn., ii. Arts. 211, 212), thus taking, as two of the variables, not Lees' λ , μ (§4), but the cosines of the angles which the fixed axis of the bearing makes with the principal axes GA, GB, of the pulley. This is virtually the same as

* Communicated by the Author.

† I may refer any one who desires a satisfactory explanation of the dynamical cause of "whirling," as free as seems possible from mathematical difficulties, to a paper by Jeffcott :—"The Lateral Vibration of Loaded Shafts," Phil. Mag. xxxvii. March 1919.

referring to axes rotating with angular velocity which is approximately constant and equal to that of the shaft.

In the diagram, which is Routh's (*l. c. i. p. 217*) with some additional letters, the origin is Lees' O_1 , the fixed point on axis of the shaft; the axes O_1X , O_1Y , O_1Z are fixed, the last being the axis of the bearing; O_1A , O_1B , O_1C are parallel to the principal axes of the pulley at its C.G., the last being perpendicular to its plane. As $X'E$ is approximately ϕ , the axes O_1X' , O_1Y' rotate with approximately constant velocity ω , that of the shaft. Relative to the fixed axes let the direction-cosines of O_1A be λ_1, μ_1, ν_1 ; of O_1B , λ_2, μ_2, ν_2 ; of O_1C , λ_3, μ_3, ν_3 . Relative to O_1X' , O_1Y' , let x', y' , be the



coordinates of the foot of the perpendicular from the C.G. of the pulley on the bent axis of the shaft, and λ', μ' , the direction-cosines of O_1C .

In the case of the pulley excentrically mounted, in estimating the restoring forces and couples, (and these are known correctly to only the first order of small quantities), it is immaterial, to the first order, whether we suppose the forces applied at the C.G. of the pulley, (Lees' G), or at the corresponding point on the axis of the shaft, (Lees' C). We have restoring forces $3 B_1(2x' - L\lambda')$ parallel to $X'O_1$, $3 B_1(2y' - L\mu')$ parallel to $Y'O_1$, and restoring couples $B_1(2L^2\mu' - 3Ly')$ about O_1X' , tending to diminish μ' , $B_1(2L^2\lambda' - 3Lx')$ about O_1Y' , tending to diminish λ' .

But λ' , or $\cos CX'$, is $\sin AX'$, and this is approximately $-\cos AZ$ or $-\nu_1$, since, in triangle $AX'Z$, $X'Z$ is $\pi/2$ and $ZX'A$ is nearly π . Similarly, $\mu' \doteq -\nu_2$.

Again, O_1X' , O_1A nearly coincide, and so do O_1Y' , O_1B ; therefore, to the first order, the moment of restoring forces round GA equals that round GX' , and similarly for GB, GY' .

Thus, if the pulley is "out of balance," we have, by resolving parallel to GX' , GY' , and taking moments round GA, GB, the equations of motion, correct to the first order,

$$M(\ddot{x}' - 2\omega\dot{y}' - \omega^2 x') + 3B_1(2x' + L\nu_1) = Mb\omega^2 \cos(\omega t + \alpha), \quad (1)$$

$$M(\ddot{y}' + 2\omega\dot{x}' - \omega^2 y') + 3B_1(2y' + L\nu_2) = Mb\omega^2 \sin(\omega t + \alpha). \quad (2)$$

$$A\dot{\omega}_1 - (B - C)\omega\omega_2 + B_1(3L\dot{y}' + 2L^2\nu_2) = 0, \quad \dots \quad (3)$$

$$B\dot{\omega}_2 - (C - A)\omega\omega_1 - B_1(3L\dot{x}' + 2L^2\nu_1) = 0, \quad \dots \quad (4)$$

ω_1 , ω_2 , being velocities about GA, GB.

Also, as ν_1 , ν_2 , ν_3 are direction-cosines with respect to the pulley of a line fixed in space, we have the kinematic equations, correct to the first order,

$$\dot{\nu}_1 - \nu_2\omega + \omega_2 = 0, \quad \dots \quad (5)$$

$$\dot{\nu}_2 - \omega_1 + \nu_1\omega = 0. \quad \dots \quad (6)$$

In these, of course, ω_3 , the velocity of the pulley round GU , has been replaced by ω , the velocity of rotation of the shaft.

Eliminating ω_1 , ω_2 , from (3)-(6), we obtain

$$A\ddot{\nu}_2 + (A + B - C)\omega\dot{\nu}_1 + (C - B)\omega^2\nu_2 + B_1(3L\dot{y}' + 2L^2\nu_2) = 0, \quad \dots \quad (7)$$

$$B\ddot{\nu}_1 - (A + B - C)\omega\dot{\nu}_2 + (C - A)\omega^2\nu_1 + B_1(3L\dot{x}' + 2L^2\nu_1) = 0, \quad \dots \quad (8)$$

For the Complementary Function, in other words for the "free" vibrations of a perfectly centred, but unsymmetrical, pulley, there are evidently solutions of the form

$$x' = X \cos(pt + \gamma), \quad y' = Y \sin(pt + \gamma), \quad \nu_1 = N_1 \cos(pt + \gamma), \\ \nu_2 = N_2 \sin(pt + \gamma), \quad \dots \quad (9)$$

where p , γ , X , Y , N_1 , N_2 , are constants.

With these substitutions the equations for the C.F. become

$$\{2B_1L^2 + (C - B)\omega^2 - Ap^2\}N_2 - (A + B - C)\omega pN_1 + 3B_1LY = 0, \quad \dots \quad (10)$$

$$\{2B_1L^2 + (C - A)\omega^2 - Bp^2\}N_1 - (A + B - C)\omega pN_2 + 3B_1LX = 0, \quad \dots \quad (11)$$

$$3B_1LN_1 + \{6B_1 - M(\omega^2 + p^2)\}X - 2M\omega pY = 0, \quad \dots \quad (12)$$

$$3B_1LN_2 + \{6B_1 - M(\omega^2 + p^2)\}Y - 2M\omega pX = 0, \quad \dots \quad (13)$$

The equation giving the "speed," p , may, therefore, be written

$$\begin{vmatrix} 2B_1L^3 + (C-B)\omega^2 - Ap^2, & 3B_1L, & -(A+B-C)\omega p, & 0 \\ 3B_1L, & 6B_1 - M(\omega^2 + p^2), & 0, & -2M\omega p \\ -(A+B-C)\omega p, & 0, & 2B_1L^2 + (C-A)\omega^2 - Bp^2, & 3B_1L \\ 0, & -2M\omega p, & 3B_1L, & 6B_1 - M(\omega^2 + p^2) \end{vmatrix} = 0. \quad (14)$$

In the treatment followed here a "whirling" speed of rotation presents itself as a value of ω for which (14) is satisfied by $p=0$. It is seen, therefore, that there are two real "whirling" speeds, each being that for the same shaft loaded with a pulley of mass M , but with moments A, A, C , in one case and B, B, C in the other. It is easily verified that, if $A < B$, the latter speed is the lower.

Proceeding to examine the nature of the "free" oscillations for other speeds of rotation, I follow Routh's argument and notation (*l. c.*, ii. Arts. 57 *et seq.*). When $p^2 = -\infty$ the signs of $\Delta, \Delta_1, \Delta_2, \Delta_3, 1$, are all positive; when $p^2 = +\infty$ they are alternately positive and negative; so that, while p^2 passes from $-\infty$ to $+\infty$, four, (the greatest number possible), changes of sign are gained. Therefore the values of p^2 given by (14) are all real, and, also, the number between $p^2 = \alpha$ and $p^2 = \beta$, where $\alpha < \beta$, is the same as the number of changes of sign in the above series which is gained as p^2 increases from α to β .

Firstly, suppose ω below both "whirling" speeds. Then, when $p^2=0$, Δ_3 is positive, since each "whirling" speed is less than the value of ω given by $\Delta_3=0$; Δ_2 also is positive, since the "whirling" speed for the shaft carrying a pulley of moments A, A, C is given by $\Delta_2=0$, and Δ_1 is positive for lower values of ω ; Δ_1 also is positive, being equal to $(6B_1 - M\omega^2)\Delta_2$; and Δ is positive, being the product of Δ_2 and a determinant which differs from Δ_2 in having A replaced by B and which, therefore, is positive. Thus there is no alternation of sign in the series $\Delta, \Delta_1, \Delta_2, \Delta_3, 1$. Consequently, all four values of p^2 given by (14) are positive.

Secondly, suppose that, A being less than B , ω exceeds the "whirling" speed for B, B, C , but is less than that for A, A, C . When p^2 is zero $\Delta_3, \Delta_2, \Delta_1$ are again positive; but Δ is negative, since it is the product of Δ_2 and a similar determinant which is now negative, however. Thus there is one alternation of sign in the series of determinants.

Consequently (14) gives one negative value of p^2 and three positive.

Thirdly, suppose that ω exceeds both "whirling" speeds but is less than $(6B_1/M)^{\frac{1}{2}}$. When p^2 is zero, Δ_3 is again positive, but Δ_2 is negative, Δ_1 is negative, and Δ is positive, being the product of Δ_2 and a similar determinant, now also negative. Thus there are two alternations of sign in the series. Consequently (14) now gives two negative values of p^2 and two positive.

Finally, suppose $\omega^2 > 6B_1/M$. When p^2 is zero, Δ_3 is now negative, Δ_2 is negative, while Δ_1, Δ are positive. Thus two alternations of sign again occur. And, therefore, again two values of p^2 are negative and two positive.

The motion is, therefore, exponentially unstable if the lower "whirling" speed is exceeded.

§ 2. *An unexplained phenomenon in a certain whirling shaft.*

I would draw attention to a phenomenon, which I cannot explain, observed in a certain whirling shaft. A model of an actual shaft was mounted by Mr. (then Prof.) Jeffcott in the Royal College of Science for Ireland and driven electrically. It had three bearings, one at each end, the other placed unsymmetrically; it carried several pulleys. Its "whirling" speed was of the order of 25 per sec.; but the amplitude of its vibrations varied regularly with a period having order of magnitude one sec.

I did not regard the vibrations of the shaft as "small"; the greatest displacement of its axis from the axis of the bearings was of the order of magnitude of the radius.

The vibrations were elliptical, not circular; Lees explains this by unsymmetrical elasticity in the bearings (see his paper, § 8, p. 698); I believe this explanation to be correct.

§ 3. *A flaw in the usual proof of stability of a system.*

In connexion with discussions of the stability of equilibrium or motion of systems in general, I have elsewhere (Proc. Royal Irish Acad. xxvii. A, 1909, pp. 12, 13, 32-36, 75) objected to the orthodox argument, that, when there is more than one coordinate, if the fundamental free disturbances are truly harmonic, or exponentially damped, then the state is certainly stable. This inference cannot be justified mathematically, even should it agree with fact in the vast majority of cases. A good deal, of course, turns on the precise meaning given to the word "stability." And the

mathematician is inclined to give it a definition which facilitates him in giving an absolute criterion; the engineer is more concerned with "safety" than with "stability." At any rate, a disturbance in which the displacement of each particle is the sum of two or more terms, each of type harmonic or damped harmonic, may be such that at some instant both the displacements and the velocities are simultaneously very great compared with their respective initial values.

I have, indeed, (*l. c.*), put this forward as an explanation of the observed instability of the motion of liquids* in certain cases. My view, however, did not commend itself to the late Lord Rayleigh.

§ 4. Absolute proofs of stability in Lees' problem.

In the problems under discussion here perfectly satisfactory proofs of stability † at all speeds with the symmetrical pulley, and under the lower "whirling" speed with the unsymmetrical, may be obtained as follows.

For the symmetrical case on multiplying Lees' equations (12)-(15) respectively by $\dot{x}$, $\dot{y}$, $\dot{\lambda}$, $\dot{\mu}$, adding, and integrating, there results

$$\frac{1}{2}M(\dot{x}^2 + \dot{y}^2) + \frac{1}{2}A(\dot{\lambda}^2 + \dot{\mu}^2) + B_1\{3(x^2 + y^2) - 3L(\lambda x + \mu y) + L^2(\lambda^2 + \mu^2)\} = \text{constant}. \quad (15)$$

The terms in B_1 are essentially positive, being, in fact, the elastic potential energy. The equation is not, however, the energy equation.

Consequently, if the steady motion receives a disturbance in which the constant has a small value C , the shaft can never bend so much that the terms in B_1 alone exceed C , nor can the value of $\dot{x}$, $\dot{y}$, $\dot{\lambda}$, or $\dot{\mu}$, exceed a definite small limit.

In the unsymmetrical case the equations of motion in Lees' coordinates give no such simple equation as (15). But, if my equations of motion, (1), (2), (7), (8), with the first two modified by replacing the right-hand member by zero, are multiplied respectively by $\dot{x}'$, $\dot{y}'$, $\dot{\nu}_2$, $\dot{\nu}_1$, and added,

* An important paper, just published, by G. I. Taylor, "Stability of a viscous fluid contained between two rotating cylinders," Phil. Trans. A. 612, appears to prove that, under certain conditions, the fundamental free disturbances are exponentially unstable, and thus to give a simpler explanation.

† That is, taking, as usual, equations of motion which are correct only to the first order of small quantities.

the resulting equation gives, on integration,

$$\begin{aligned} \frac{1}{2}M(\dot{x}'^2 + \dot{y}'^2) + \frac{1}{2}(A\dot{v}_2'^2 + B\dot{v}_1'^2) + \left(3B_1 - \frac{M\omega^2}{2}\right)(x'^2 + y'^2) \\ + 3B_1L(v_1x' + v_2y') + \left(B_1L^2 + \frac{C-B}{2}\omega^2\right)v_2'^2 \\ + \left(B_1L^2 + \frac{C-A}{2}\omega^2\right)v_1'^2 = \text{constant.} \dots \dots (16) \end{aligned}$$

In the expression on the left the terms which involve the coordinates are not positive for all values of ω . But whenever they are the same argument as was applied to (15) furnishes an absolute proof of stability. The necessary and sufficient conditions are that the terms in x' and v_1 should be positive, and also those in y' and v_2 . The second of these conditions is

$$(6B_1 - M\omega^2)\{2B_1L^2 + (C-B)\omega^2\} - 9B_1^2L^2 > 0, \dots (17)$$

i. e., that ω is less than the "whirling" speed with the symmetrical pulley of moments B, B, C ; and the first is similarly that ω is less than that for the pulley of moments A, A, C . If ω is so limited, then, the motion is certainly stable.

And the "speed" equation has shown that, if ω exceeds such a limit, the motion is certainly unstable.

Equation (16) holds in the case of symmetry also. It is another integral of the equations of motion, independent of (15). But it does not serve to prove, as (15) does, that the motion is stable at all speeds.

A similar proof of absolute stability at all speeds in the case of elastic yielding discussed by Lees is easily obtained from his equations (34).

In the R. I. A. paper referred to I took as an instance of the weakness of the orthodox argument for stability an unsymmetrical top, properly chosen, and examined it in some detail. I now add that, in that case, we may easily obtain an equation of a type differing from (15) and (16) in having as the left-hand side the *difference*, instead of the *sum*, of two quadratic functions, each essentially positive, one involving the velocities and the other the coordinates.

LXVIII. *On the Theory of the Characteristic Curve of a Photographic Emulsion.*—Part II. By F. C. TOY, D.Sc., F.Inst.P.*

[Communication No. 27 from the British Photographic Research Association Laboratory.]

IN a previous paper (Phil. Mag. 1922, xliv. pp. 352–371) it has been shown that for a fast emulsion the relation which is found to hold experimentally between the number of geometrically identical silver halide grains made developable and the light-intensity, is in qualitative agreement with the assumption that there exist in the grains specially light-sensitive points. These are distributed amongst the grains according to the laws of chance, and only grains which have at least one will be developable. The action of the light changes their condition in such a way that they become susceptible to the action of the developer and cause the reduction of the silver halide in their neighbourhood and hence ultimately of the whole grain. It is assumed that each nucleus does not necessarily require the same intensity to change it. The effect of variation of grain size is discussed, and it is shown that the experimental facts do not admit of the assumption regarding the similarity of the light-sensitive material in grains of various sizes in the case of a highly sensitive emulsion. The question of the validity of this assumption under any circumstances is obviously of great importance for the theory of the photographic process, and the evidence existing in its favour must now be closely examined.

The assumption was made by Svedberg (Phot. Journ. 1922, lxii. pp. 186–192, 310–320) that “the small and the larger grains in one and the same emulsion are built up of the same kind of light-sensitive material—just as if they were fragments of different size from one homogeneous silver bromide crystal.” He says (p. 317) that for this hypothesis to be true a relationship which must hold is that

$$\nu_1/a_1 = \nu_2/a_2 = \dots = c = \text{constant}, \quad \dots (8)$$

where $\nu_1, \nu_2, \dots$ are the average number of centres per grain (which we have previously denoted by N_0), $a_1, a_2, \dots$ are the areas of the surfaces of the spherical grains of the emulsion

* Communicated by Prof. A. W. Porter, F.R.S.

used, and c the average number of centres per square centimetre of grain surface. Considering only two sizes of grains, we have from (8),

$$\nu_2/\nu_1 = a_2/a_1, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

i. e. the ratio of the average number of nuclei per grain for two sizes of grain is constant and equal to the ratio of the surface areas. *It is therefore independent of the exposure.*

Let us now examine the experimental evidence which is taken by Svedberg as supporting this hypothesis. The data given by him in support of the validity of equation (8) have been rearranged in Tables I. and II. so as to show to what extent they support equation (9). The first column in Table I. gives the average area of grain for three different sizes, and the second and third columns the average number of nuclei per grain occurring at two different intensities (I). In Table II. the ratios of these numbers are calculated.

TABLE I.

Average area of grain.	I=1.00.	I=1.56.
24.2×10^{-9} cm. ²	$\nu_1=0.48$	$\nu_1=0.94$
46.5×10^{-9} cm. ²	$\nu_2=0.82$	$\nu_2=1.90$
78.1×10^{-9} cm. ²	$\nu_3=1.47$	$\nu_3=2.59$

TABLE II.

I=1.00.	I=1.56.
$\nu_2/\nu_1=1.71$	$\nu_2/\nu_1=2.02$
$\nu_3/\nu_1=3.06$	$\nu_3/\nu_1=2.76$
$\nu_3/\nu_2=1.79$	$\nu_3/\nu_2=1.36$

Whether these figures may be taken as supporting the hypothesis is certainly open to doubt, for the following reasons :—

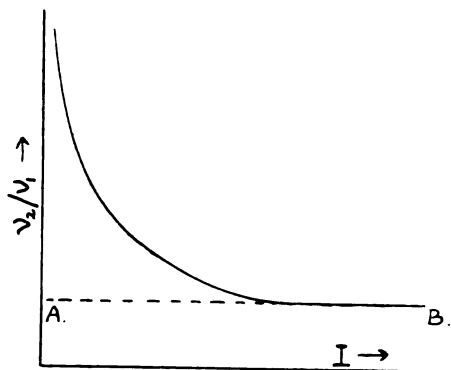
(1) The value of ν_2/ν_1 ... etc., actually varies considerably with the exposure, the difference between the pairs of values given being of the order of 18, 10, and 24 per cent.

(2) These are values obtained only over a small range of intensities. The characteristic curve of the emulsion used extends over a range of intensities of about 1 to 5, so that these results are confined to a small part of the curve. Thus the experimental results seem to be very slender evidence in support of the hypothesis.

It was predicted in Part I. that the ratio ν_2/ν_1 will not be constant, but will vary with the intensity. When this is small the ratio will be very large and may become infinite, and as the intensity is increased ν_2/ν_1 decreases, at first rapidly, and ultimately approaches a constant value as more and more of the nuclei are affected. If, therefore, we plot ν_2/ν_1 against the intensity we expect to obtain the kind of

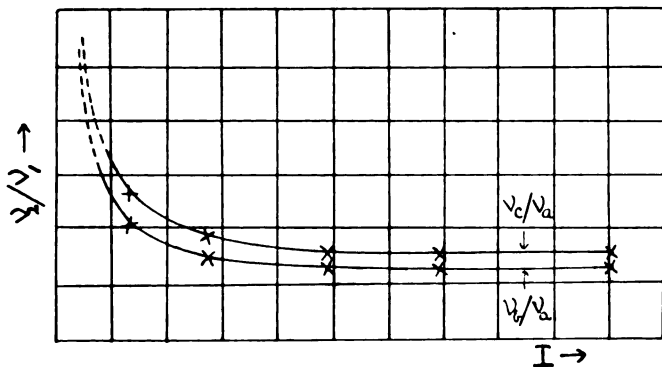
curve in fig. 1. On Svedberg's assumption we should simply get a straight line such as A B parallel to the I axis.

Fig. 1.



In the case of high speed emulsions it has already been shown that ν_2/ν_1 is not independent of the exposure but, at the lower intensities, varies enormously with it. This is shown in fig. 2, where the curves are obtained from some of the data published in Part I. (p. 365). The similarity with the theoretical curve in fig. 1 is at once apparent.

Fig. 2.



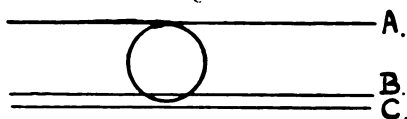
As has been shown in the first paper, this variation of the number of nuclei with the exposure is easily explained if we assume that the reason why large grains are more sensitive than small ones is not only that there exist more nuclei in the larger grains, but also that the average sensitivity of the nuclei increases with the grain size. Thus in the case of high-speed emulsions the different grains can by no means

be looked upon as "fragments of different size from one homogeneous silver bromide crystal"; rather must we regard the sensitive material as having, on the average, the same characteristics only for classes of equal-sized grains, and varying enormously from one class to another. This result is probably bound up with the ripening process.

If Svedberg's hypothesis that grains of all sizes contain the same kind of light-sensitive material were true for slow, spherical grains, then there must be some fundamental difference in the process of formation of the nuclei in slow and fast emulsions. It was, therefore, considered very important to test this hypothesis for a process emulsion over the whole range of its characteristic curve.

It was not possible to work with the same emulsion as Svedberg used, which was specially prepared by Messrs. Ilford Ltd. The nearest which could be obtained was the Ilford Process Emulsion, which is, however, the same type, the main difference apparently being that in the special emulsion the grain size is more uniform than in the ordinary process plates. Special "single layer" plates were made up in the usual way, and the exposure was made behind a step-wedge to white light. The plate was then developed to completion, washed, and dried without fixing. The method of measurement was practically the same as described in the previous paper. Two sizes of grain were selected for the experiment, one size (class 1) having a diameter of $(0.60 \pm 0.05)\mu$, and the other (class 2) a diameter of $(0.75 \pm 0.05)\mu$. Photo-micrographs of the emulsion were taken, over the whole range of the characteristic curve, on Barnet ortho process plates at a magnification of 2000, using a 2 mm. objective, a $\times 14$ eyepiece, monochromatic green light, and N.A. 1.4. The negatives were then optically

Fig. 3.



projected on to a screen at a magnification of 5. The grains counted in class 1 were those whose images just fitted between parallel lines drawn on a white card, as in fig. 3, in such a way that $AB < d < AC$, where d is the diameter of the grain, and AB and AC are equal to 5.5 mm. and 6.5 mm. respectively.

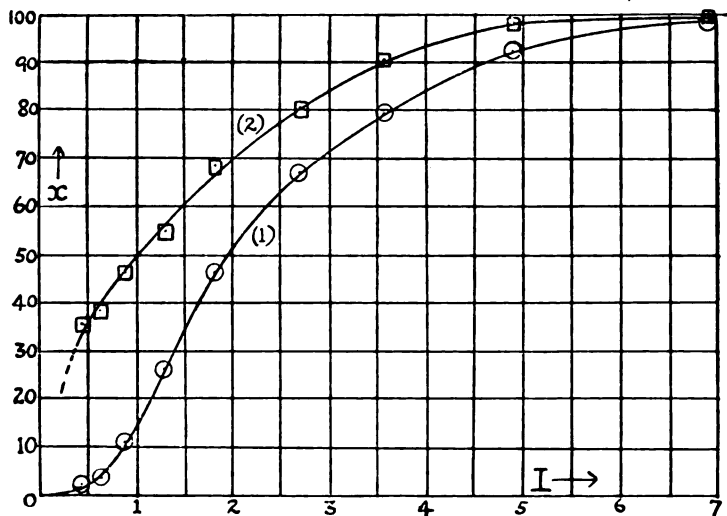
The method of counting previously described was modified

so as to eliminate any error due to fog and unevenness of coating. Let the total number of all sizes of grains, developed and undeveloped, in an arbitrary area of the unexposed portion of the plate be x_0 , and the number of undeveloped grains of class 1 be y_0 . Then the ratio of the number of undeveloped grains of class 1 to the total number of grains for the fogged portion of the plate is y_0/x_0 , and this is independent of variations in the number of grains per unit area due to an uneven coating. In a certain area of the exposed part of the plate (which need not be the same as the area in the fogged portion) let the total number of grains of all sizes, developed and undeveloped, be x_e , and the total undeveloped of class 1 be y_e . Then, if this part of the emulsion had not been exposed, the number of grains of class 1 would have been $y_0 x_e / x_0$. Thus the number of class 1 which have been changed by the light-action is

$$y_0 x_e / x_0 - y_e,$$

out of a total of $y_0 x_e / x_0$ unaffected by fog.

Fig. 4.



Therefore the percentage changed (x) due to the light-action only is given by

$$x = 100 [1 - y_e x_0 / y_0 \cdot x_e]. \quad (10)$$

The values of x (x_1 and x_2) obtained from equation (10) for the two classes of grain are plotted in fig. 4, and the smooth curve values, together with the corresponding values

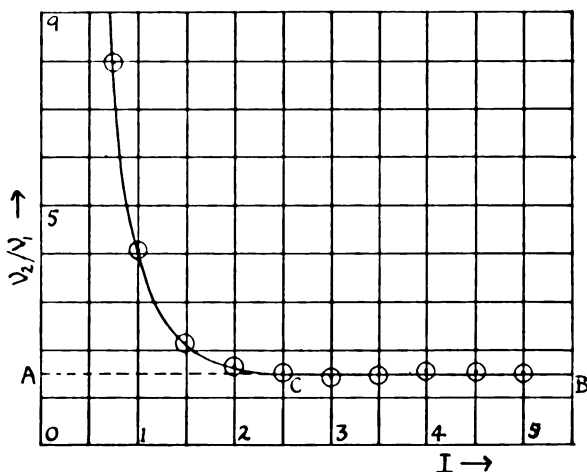
of ν_1 and ν_2 and the ratio ν_2/ν_1 , are given in Table III. The values of ν are calculated from the relation (found in Part I.), $\log [100/(100-x)] = \nu$.

TABLE III.

I.	x_1 .	x_2 .	ν_1 .	ν_2 .	ν_2/ν_1 .
0.500	93.5	98.5	2.734	4.200	1.54
0.450	89.8	97.0	2.271	3.507	1.54
0.400	84.5	94.6	1.865	2.917	1.56
0.350	79.0	90.0	1.561	2.303	1.48
0.300	73.0	84.2	1.309	1.843	1.41
0.250	63.5	78.0	1.009	1.514	1.51
0.200	52.0	70.5	0.734	1.221	1.67
0.150	35.5	61.5	0.438	0.956	2.18
0.100	16.0	50.8	0.174	0.709	4.07
0.075	7.0	44.0	0.073	0.580	7.96
0.050	2.0	35.5	0.020	0.438	21.90

The values of ν_2/ν_1 are plotted against the intensity in fig. 5, and it will be seen that the curve is of exactly the

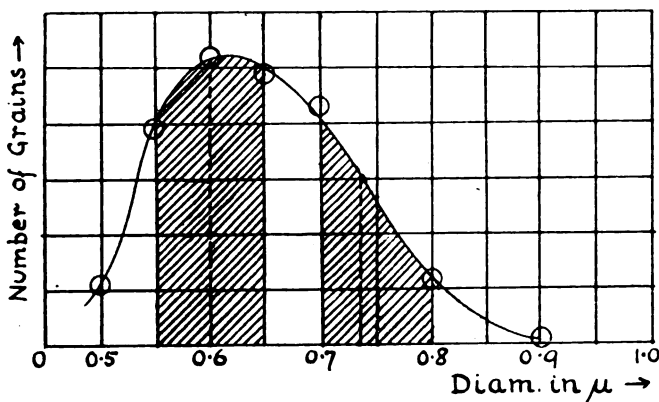
Fig. 5.



same form as in the case of a fast emulsion. Now Svedberg has proved that for a process emulsion with spherical grains all the nuclei are on the surface, so that when all the nuclei are operative (*i. e.* when I is large) we should expect the constant value to which ν_2/ν_1 approaches to be the ratio of the surfaces of the two classes of grain. A fairly accurate

value of this can be very easily found. We are not justified in taking this ratio as exactly $(7.5)^2/(6.0)^2$ unless there are just as many grains between $0.55-0.60\mu$ and $0.70-0.75\mu$ as there are between $0.60-0.65\mu$ and $0.75-0.80\mu$ respectively. In fig. 6 are plotted as ordinates the relative numbers of grains having fixed diameters. We have to take as the average of the diameters those values such that the ordinates through them divide the areas under the curve between the limits $0.55 < \mu < 0.65$ and $0.70 < \mu < 0.80$ into two equal parts.

Fig. 6.



These are found with sufficient accuracy to be 0.600μ and 0.735μ . Thus the theoretical ratio which ν_2/ν_1 approaches is

$$(7.35/6)^2 = 1.50,$$

and this is the value obtained experimentally as near as it can be determined from the curve in fig. 5.

If the hypothesis of the similarity of the light-sensitive material in both classes of grain were true then the curve obtained in fig. 5 would be the straight line BCA. Thus it appears that the two intensities which Svedberg used were somewhere on the BC portion of the curve, which would explain the constancy, and the value, of the ratio ν_2/ν_1 which he found.

If, therefore, equation (9) is a necessary consequence of Svedberg's hypothesis, we are led to conclude that

- (1) In any particular emulsion, whether fast or slow, the photosensitive material gives the same average response to light only in grains of the same size.
- (2) This response increases continuously with the grain size. As has been suggested, the explanation of this is probably intimately connected with the ripening process.

Svedberg has shown that in the case of spherical grains the nuclei which show up on partial development are, on the average, distributed equally over the grain surface; the author's results prove that for flat grains they occur more on the edges than anywhere else. To explain this it might be considered natural to attribute it to the existence of protuberances and sharp edges at which, the solution pressure being higher, the reaction will be facilitated. On this supposition the nuclei are not specially sensitive points at all, but are simply a result of the attack of the developer on the grain. This possibility has been mentioned in Part I. (p. 370), but the argument against it was not fully dealt with there. Obviously it is exceedingly important to settle this question, because if it were true that the nuclei observed are only due to the developer, then the whole argument in favour of specially sensitive points fails. The argument is based on the manner in which the average number of nuclei per grain varies with the intensity.

At a certain exposure the actual numbers of nuclei which were found on the members of a group of 50 equal-sized triangular flat grains were as follows:—

1211224110024112132041111

1200211123103201322232121.

The total number of nuclei is 77, made up of three 4's, five 3's, fifteen 2's, twenty 1's, and seven zeros. The average per grain, *counting every grain*, is $77/50 = 1.54$, which has already been denoted by ν . The seven zeros represent the seven grains which are undevelopable because they have not got a nucleus. The average for 43 developable grains, which we will call ν_d , is $77/43 = 1.79$. Now, if the nuclei which are found on partial development of developable grains are the result of the action of the developer upon specific points determined solely by the geometrical formation of the crystals, then ν_d should be constant for all exposures for a given geometrical character of the crystal. The only reason why ν decreases with a decrease of exposure would, on this assumption, be that there is an increase in the percentage of zeros. Starting with the experimental values given above, the kind of results which would be obtained is illustrated by the fictitious set of figures in Table IV. arranged in order of decreasing exposure.

TABLE IV.

Distribution of Nuclei.	ν .	ν_d .
1211224110024112132041111 }	1.54	1.79
1200211123103201322232121 }		
0124300121100011111200200 }	1.03	1.80
0342220020001122020200113 }		
0001002000400100100011300 }	0.72	1.80
0011010000300012202212022 }		
0000001000200001030000210 }	0.36	1.80
0000000202000000031000000 }		

Here ν_d is constant and ν decreases with the exposure only because the percentage of zeros increases.

On the other hand, if the theory of "preference" points is true, then, as the exposure decreases, ν_d should also decrease down to a limiting value of unity. Now a set of figures which was actually obtained in an experiment is given in Table V., and it will be seen to be exactly as predicted by this theory. Such a result can be repeated any number of times, and would be practically impossible if the nuclei were due only to the action of the developer.

TABLE V.

Distribution of Nuclei.	ν .	ν_d .
1211224110024112132041111 }	1.54	1.79
1200211123103201322232121 }		
2201111111311210003112220 }	1.24	1.51
2101110112112012103311222 }		
0021121110000110121100001 }	0.76	1.31
1220110200011020021110210 }		
0110010010001001000101000 }	0.42	1.17
1000012002000100011101002 }		

There remains, as a serious alternative to the theory of specially sensitive points, the theory, put forward by Silberstein, and based on the idea of the bombardment of the grains by discrete light quanta (Phil. Mag. 1922, xlv. pp. 257, 956). Experimental results which are brought forward as supporting the theory are given by Trivelli and Righter (Phil. Mag. 1922, xlv. p. 252). The interpretation of these results has already been briefly criticized by the author (B. J. P. 1922, lxix. pp. 443-444). It is proposed now to summarize, as concisely as possible, the evidence for and against this light-quantum theory.

The fundamental equation, which Silberstein says is of

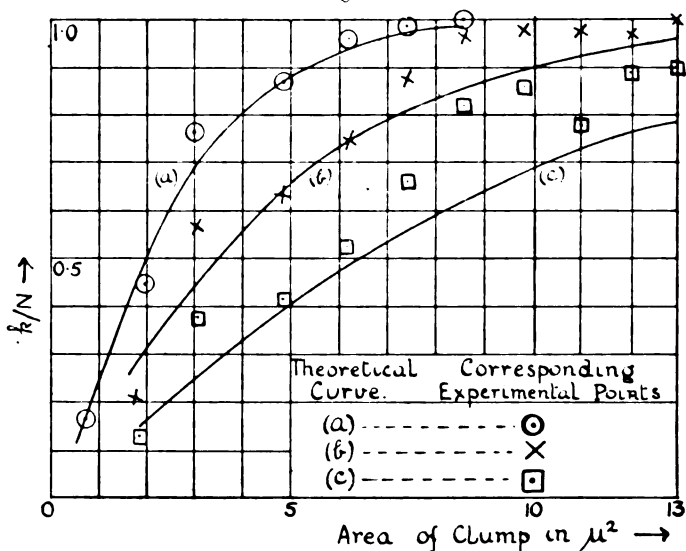
more than sufficient mathematical accuracy under the conditions prevailing in all practicable experimental cases, is

$$k/N = 1 - e^{-na}, \quad (11)$$

where a is the projected area of the grain, k the number of grains hit, N the total number of grains per unit area, and n the number of light-quanta impinging upon unit area.

Now, Trivelli and Richter have found that in *certain cases* where the grains of an emulsion are grouped together in clumps the whole of the clump acts as a single grain for development to the limit, i. e., the sufficient condition for the whole clump to be reduced is that one grain in it has been changed by the light. Admittedly this fact is proved by Trivelli's recent communication (B. J. P. 1922, lxix. p. 687).

Fig. 7.



Having proved this for a particular emulsion they proceed, with it, to test equation (11) for *clumps* of grains, rather than for single grains, on the ground that this will provide a much more severe test because a much bigger variation in a can thus be obtained. The agreement between the theoretical and observed values for three cases which are given, is shown in fig. 7, and, at all events as regards cases (b) and (c), it is difficult to take it as proved that the experimental results are in accordance with equation (11) in the case of clumps. Especially is this so in view of the fact

that the only point of agreement—viz., that the average experimental value of k/N does certainly increase with a as does the theoretical value—is what is to be expected on the theory of specially sensitive points.

When we come to test the equation in the simplest possible cases, we find that it breaks down completely. For example, it will not fit, even approximately, the curves given in this paper or in Part I. for sets of equal-sized grains. Again, if we consider the case of two sets of grains of different sizes we have:—

$$\log (N/(N-k_1)) = na_1 \quad \text{and} \quad \log (N/(N-k_2)) = na_2.$$

The left-hand side of the equation has already been shown to be equal to ν , so that

$$\nu_1 = na_1 \quad \text{and} \quad \nu_2 = na_2,$$

$$\text{or} \quad \nu_2/\nu_1 = a_2/a_1 = \text{constant},$$

which is the same condition as required by Svedberg's hypothesis, and which has been shown to be untenable.

In discussing the dependence of the photographic effect on the wave-length, Silberstein deduces the equation (p. 266)

$$s = \beta E \cdot a\lambda, \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where E is the incident light-energy (exposure), λ the wave-length of the monochromatic light, β a constant, and $s=na$. But, from equation (11),

$$na = \log [N/(N-k)] = A.$$

$$\therefore A = \beta E \cdot a\lambda.$$

Thus for a constant value of a and E , we have

$$A \propto \lambda,$$

i. e., A would "increase steadily with the wave-length of the incident light up to the photoelectric critical value λ_c and then drop suddenly to zero." Silberstein goes on to say that this abrupt drop to zero might only occur in a set of equal-sized grains, since grains of different sizes may have different values of λ_c . "For then, although the curve of each grain class would end abruptly, the superposition of such curves ending over a range of different abscissæ might properly displace and smooth out the resultant maximum." This question of maximum and the manner in which the A, λ curve drops to zero need not be considered

here, since the maximum cannot be reached until the wave-length is long enough to include some of the critical frequencies. In the author's experiments now to be described, and which have not yet been published, this state was never reached, so that according to Silberstein A should vary strictly as λ . The experimental method was as follows:—Sections of a single layer Ilford process emulsion were exposed for equal times to the same incident intensity (as measured by a thermopile) of different monochromatic lights. The source was the mercury arc, and the wave-lengths used were $\lambda_1=436$ and $\lambda_2=406$ (mean of 405 and 408). Therefore the ratio of A_1/A_2 ought to have been about $44/41=1.07$. The ratios found in three different cases were 0.40, 0.36, and 0.37. Therefore instead of becoming greater, A decreases very rapidly as the wave-length increases.

All these experiments go to show that a relation of the type of equation (11) is fundamentally wrong as expressing the true mechanism of photographic exposure. This is what Slade and Higson concluded (Proc. Roy. Soc. 1920, A, xcviii. p. 154) over three years ago.

In conclusion, the author wishes to express his thanks to Dr. Slater Price (Director of Research of the British Photographic Research Association) and to Professor Porter for their interest in this work.

LXIX. *The Gravitational Field of a Particle on Einstein's Theory.* By J. T. COMBRIDGE, B.A., University of London, King's College *.

§ 1. **T**HE most general form for the line-element in a static gravitational field symmetrical about the origin is

$$ds^2 = -e^{\lambda} dr^2 - e^{\mu} (r^2 d\theta^2 + r^2 \sin^2 \theta d\phi^2) + e^{\nu} dt^2, \quad (1.0)$$

where λ , μ , and ν are functions of r only.

It is well known that the equations of the gravitational field are insufficient to determine λ , μ , and ν , and the general procedure has been to assume some relation between them, as, for example, $\lambda=0$ †, $\mu=0$ ‡, $\lambda-\mu=0$ §, $\lambda+2\mu+\nu=0$ ||.

This lack of determinacy is due to the fact that the

* Communicated by Prof. G. B. Jeffery.

† J. Droste, Proc. Amsterdam Acad. vol. xix.

‡ Schwarzschild, *Sitzungsber. Ber.* 1916, Feb.

§ F. W. Hill and G. B. Jeffery, Phil. Mag. Ser. 6, vol. xli., and an approximate solution by de Sitter, Proc. Amst. Acad. vol. xix.

|| Einstein, *Sitzungsber. Ber.* 1915, Nov.

condition of symmetry about the origin imposes on the measurement of the coordinate r no other condition than that whatever be the mode of measurement in one radial direction the same mode must be adopted in every other radial direction. Subject to this condition, any function of r may be taken as the coordinate instead of r , the substitution of this function in (1.0) giving, of course, a different form for ds^2 .

The purpose of this note is to show explicitly how this indeterminacy arises in the solution of the field equations, and to determine the λ , μ , and ν of equation (1.0) in terms of a single arbitrary function. The notation adopted is that employed by Eddington in his "Report on the Relativity Theory of Gravitation."

§ 2. We take the line-element to be of the form

$$ds^2 = -e^\lambda dr^2 - e^\mu r^2 d\theta^2 - e^\mu r^2 \sin^2 \theta d\phi^2 + e^\nu dt^2, \quad (2.0)$$

where λ , μ , ν are functions of r only, and we try for a solution of

$$G_{\sigma\tau} \equiv \{\sigma\alpha, \beta\}\{\tau\beta, \alpha\} - \frac{\partial}{\partial x_\alpha}\{\sigma\tau, \alpha\} - \{\sigma\tau, \alpha\} \frac{\partial}{\partial x_\alpha} (\log \sqrt{-g}) \\ + \frac{\partial^2}{\partial x_\sigma \partial x_\tau} (\log \sqrt{-g}) = 0.$$

From (2.0) we have

$$\begin{aligned} g_{11} &= -e^\lambda, & g_{33} &= -r^2 \sin^2 \theta e^\mu, \\ g_{22} &= -r^2 e^\mu, & g_{44} &= e^\nu, \\ g_{\sigma\tau} &= 0 \text{ if } \sigma \neq \tau, \\ g &= -r^4 \sin^2 \theta e^{\lambda+2\mu+\nu}. \end{aligned}$$

The Christoffel Symbols which do not vanish are :

$$\begin{aligned} \{11, 1\} &= \frac{1}{2}\lambda', \\ \{12, 2\} &= \frac{1}{2r}(\mu'r + 2), & \{22, 1\} &= -\frac{1}{2}r(\mu'r + 2)e^{\mu-\lambda}, \\ \{13, 3\} &= \frac{1}{2r}(\mu'r + 2), & \{33, 1\} &= -\frac{1}{2}r(\mu'r + 2)\sin^2 \theta e^{\mu-\lambda}, \\ \{14, 4\} &= \frac{1}{2}\nu', & \{44, 1\} &= \frac{1}{2}\nu'e^{\nu-\lambda}, \\ \{23, 3\} &= \cot \theta, & \{33, 2\} &= -\sin \theta \cos \theta, \end{aligned}$$

where dashes denote differentiation with respect to r , as, indeed, they will throughout.

Omitting terms which vanish, and taking account of the fact that, although its terms do not all vanish separately, yet

$$G_{12} \equiv 0 \quad \text{identically,} \quad \text{and that}$$

$$G_{33} \equiv \sin^2 \theta G_{22},$$

we get three equations, from $G_{11}=0$, $G_{22}=0$, $G_{44}=0$, respectively. They are * :—

$$\mu'' + \frac{1}{2}\nu'' + \frac{1}{2}\mu'^2 + \frac{1}{4}\nu'^2 - \frac{1}{2}\lambda'\mu' - \frac{1}{2}\lambda'\nu' - \frac{1}{r}\lambda' + \frac{2}{r}\mu' = 0,$$

$$\mu'' + \mu'^2 - \frac{1}{2}\lambda'\mu' + \frac{1}{2}\mu'\nu' - \frac{1}{r}\lambda' + \frac{4}{r}\mu' + \frac{1}{r}\nu' = \frac{2}{r^2}(e^{\lambda-\mu}-1),$$

$$-\frac{1}{2}\nu'' - \frac{1}{4}\nu'^2 - \frac{1}{2}\mu'\nu' + \frac{1}{4}\lambda'\nu' - \frac{1}{r}\nu' = 0.$$

These can be combined to give

$$\mu'' - \frac{1}{2}\lambda'\mu' + \frac{1}{2}\mu'^2 - \frac{1}{2}\mu'\nu' - \frac{1}{r}\lambda' + \frac{2}{r}\mu' - \frac{1}{r}\nu' = 0,$$

$$\nu'' + \frac{1}{2}\nu'^2 + \mu'\nu' - \frac{1}{2}\lambda'\nu' = 0,$$

$$\frac{1}{2}\mu'^2 + \mu'\nu' + \frac{2}{r}\mu' + \frac{2}{r}\nu' + \frac{2}{r^2} = \frac{2}{r^2}e^{\lambda-\mu},$$

which may be reduced to

$$\frac{\partial}{\partial r} \left\{ r e^{-\frac{1}{2}(\lambda-\mu+\nu)} \frac{\partial \mu}{\partial r} \right\} + 2 \frac{\partial}{\partial r} \left\{ e^{-\frac{1}{2}(\lambda-\mu+\nu)} \right\} = 0, \quad (2.1)$$

$$\frac{\partial}{\partial r} \left\{ r^2 e^{-\frac{1}{2}(\lambda-2\mu-\nu)} \frac{\partial \nu}{\partial r} \right\} = 0, \quad (2.2)$$

$$(\mu'r + 2)(\mu'r + 2 + 2\nu'r) = 4e^{\lambda-\mu}. \quad (2.3)$$

§ 3. Integrating (2.1) and (2.2) we have

$$\mu'r + 2 = b e^{\frac{1}{2}(\lambda-\mu+\nu)}, \quad (3.11)$$

$$\nu'r^2 = a e^{\frac{1}{2}(\lambda-2\mu-\nu)}, \quad (3.12)$$

where a and b are constants of integration.

Now (3.11) may be written

$$\frac{\partial}{\partial r} (r e^{\frac{1}{2}\mu}) = \frac{1}{2} b e^{\frac{1}{2}(\lambda+\nu)},$$

from which it may be seen that, if we make the boundary

* Compare de Sitter, Monthly Notices R. A. S. vol. lxxvi. p. 712.

conditions at infinity such that λ , μ and $\nu \rightarrow 0$ as $r \rightarrow \infty$, then we must have $b=2$.

In (3.11) and (3.12) make the substitution

$$re^{\frac{1}{2}\mu} = f(r) \equiv f.$$

Then

$$e^{\frac{1}{2}(\lambda+\nu)} = f', \quad . \quad . \quad . \quad . \quad . \quad (3.21)$$

$$e^{\frac{1}{2}(\lambda-\nu)} = \nu' f^2 / a. \quad . \quad . \quad . \quad . \quad . \quad (3.22)$$

Eliminating e^λ ,

$$\nu' e^\nu = a f' / f^2,$$

so that

$$e^\nu = 1 - \frac{a}{f}, \quad . \quad . \quad . \quad . \quad . \quad (3.3)$$

the constant of integration having been adjusted so that $\nu \rightarrow 0$ as $r \rightarrow \infty$.

Putting this value of e^ν in (3.21) we find that

$$e^\lambda = \frac{f'^2}{1 - a/f} \quad . \quad . \quad . \quad . \quad . \quad (3.4)$$

with

$$e^\mu = \frac{f'^2}{r^2} \quad . \quad . \quad . \quad . \quad . \quad (3.5)$$

Thus from equations (2.1) and (2.2) we have λ , μ , and ν in terms of a single function f . On substituting in (2.3) we find that, instead of giving an equation to find f , (2.3) is satisfied identically, showing that $f(r)$ is an arbitrary function of r .

Eliminating f between (3.3) and (3.5) we have

$$e^\nu = 1 - \frac{a}{r} e^{-\frac{1}{2}\mu},$$

and we conclude that the equations

$$G_{\sigma r} = 0$$

will be satisfied so long as this relation between μ and ν is satisfied.

§ 4. Our line-element is therefore of the form

$$ds^2 = -e^\lambda dr^2 - f^2(d\theta^2 + \sin^2\theta d\phi^2) + e^\nu dt^2, \quad . \quad (4.0)$$

where f is an arbitrary function of r , and e^λ and e^ν are functions of f which are given explicitly in equations (3.4) and (3.3) but have been retained here for brevity. This form

730 Mr. J. T. Combridge on the Gravitational
 was derived by Droste and Schwarzschild from the equation

$$\delta \iiint G \sqrt{-g} dx_1 dx_2 dx_3 dx_4 = 0.$$

The Christoffel Symbols which do not vanish are now:—

$$\begin{aligned} \{11, 1\} &= \frac{1}{2}\lambda', \\ \{12, 2\} &= f'/f & \{22, 1\} &= (f-a)/f', \\ \{13, 3\} &= f'/f & \{33, 1\} &= \sin^2 \theta (f-a)/f', \\ \{14, 4\} &= \frac{1}{2}\nu' & \{44, 1\} &= \frac{1}{2}\nu' e^{\nu-\lambda}, \\ \{23, 3\} &= \cot \theta & \{33, 2\} &= -\sin \theta \cos \theta. \end{aligned}$$

The equations of motion of a particle moving in this field are

$$\frac{\partial^2 x_\sigma}{\partial s^2} + \{\alpha\beta, \sigma\} \frac{\partial x_\alpha}{\partial s} \frac{\partial x_\beta}{\partial s} = 0;$$

that is,

$$\begin{aligned} \frac{d^2 r}{ds^2} + \frac{1}{2}\lambda' \left(\frac{dr}{ds}\right)^2 + \frac{f-a}{f'} \left(\frac{d\theta}{ds}\right)^2 + \frac{f-a}{f'} \sin^2 \theta \left(\frac{d\phi}{ds}\right)^2 \\ + \frac{1}{2}\nu' e^{\nu-\lambda} \left(\frac{dt}{ds}\right)^2 = 0, \quad (4.1) \end{aligned}$$

$$\frac{d^2 \theta}{ds^2} + \frac{2f'}{f} \frac{dr}{ds} \frac{d\theta}{ds} - \sin \theta \cos \theta \left(\frac{d\phi}{ds}\right)^2 = 0, \quad (4.2)$$

$$\frac{d^2 \phi}{ds^2} + \frac{2f'}{f} \frac{dr}{ds} \frac{d\phi}{ds} + 2 \cot \theta \frac{d\theta}{ds} \frac{d\phi}{ds} = 0, \quad (4.3)$$

$$\frac{d^2 t}{ds^2} + \nu' \frac{dr}{ds} \frac{dt}{ds} = 0. \quad (4.4)$$

If initially the particle moves in the plane $\theta = \frac{\pi}{2}$ so that initially $\frac{d\theta}{ds} = 0$, then, from (4.2),

$$\frac{d^2 \theta}{ds^2} = 0,$$

and so $\frac{d\theta}{ds} = 0$ always. Hence (4.3) and (4.4) simplify, and integrate to give

$$f^2 \frac{d\phi}{ds} = \text{const.} = h, \quad (4.5)$$

$$e^\nu \frac{dt}{ds} = \text{const.} = k. \quad (4.6)$$

Instead of using (4.1) with these we use (4.0), which reduces to

$$\left(\frac{dr}{ds}\right)^2 + \frac{f(f-a)}{f'^2} \left(\frac{d\phi}{ds}\right)^2 = \frac{k^2}{f'^2} - \frac{f-a}{ff'^2},$$

i. e. $f'^2 \left(\frac{dr}{ds}\right)^2 + f^2 \left(\frac{d\phi}{ds}\right)^2 = k^2 - \frac{f-a}{f} + af \left(\frac{d\phi}{ds}\right)^2,$

i. e. $\left(\frac{df}{ds}\right)^2 + f^2 \left(\frac{d\phi}{ds}\right)^2 = k^2 - 1 + \frac{a}{f} + \frac{ah^2}{f^3}.$

§ 5. It is interesting to note how solutions previously found by making *a priori* assumptions as to the indeterminacy of the line-element may be obtained from the results of § 3.

When we take $\mu=0$, then $f=r$, and, writing $2m$ instead of a , the constant of integration, we have from (3.3) and (3.4),

$$e^v = 1 - \frac{2m}{r},$$

$$e^\lambda = e^{-v}.$$

When we take $\lambda=\mu$ we have, from (3.4) and (3.5), a differential equation in f :—

$$r^2 f'^2 = f(f-a),$$

the solution of which is

$$f = \frac{a(r+a_1)^2}{4a_1 r}.$$

If we determine a_1 , the constant of integration, by noting that

$$e^{4\mu} = \frac{f}{r} = \frac{a}{4a_1} \left(1 + \frac{a_1}{r}\right)^2,$$

and by the condition that $\mu \rightarrow 0$ as $r \rightarrow \infty$, we find that

$$4a_1 = a,$$

$$\frac{f}{r} = \left(1 + \frac{a}{4r}\right)^2.$$

Writing again $2m$ instead of a we get

$$e^\lambda = e^\mu = \left(1 + \frac{m}{2r}\right)^4,$$

$$e^v = \left(\frac{1 - \frac{m}{2r}}{1 + \frac{m}{2r}}\right)^2.$$

The condition $\lambda + 2\mu + \nu = 0$ is seen to be equivalent to the condition $\mu = 0$, for, from (3.3), (3.4), and (3.5),

$$e^{\lambda+2\mu+\nu} = \frac{f^4 f'^2}{r^4},$$

so that $\lambda + 2\mu + \nu = 0$ means

$$f^4 f'^2 = r^4,$$

whence

$$f = \pm r,$$

and since $r^2 e^\mu = f'^2$, the result follows.

LXX. On the Inversion of Bernoulli's Theorem.

By CHARLES JORDAN *.

1. SUPPOSING that a certain phenomenon could have taken place in one, and only one, of several different ways; let us denote by ω_i the probability *a priori* (i. e. before the phenomenon has occurred) that the *i*th way is followed, and by P_i the probability that in this case the phenomenon occurs. The probability *a posteriori* ΔW_i (i. e. after the event) that the phenomenon has been obtained in the *i*th way is given by Bayes' Theorem:

$$\Delta W_i = \frac{\omega_i P_i}{\sum \omega_i P_i} \cdot \cdot \cdot \cdot \cdot \cdot (1)$$

If ω_i and P_i are given quantities, no objection at all can be made to this formula.

Often P_i is given while ω_i is unknown; then we must adopt some hypothesis concerning the values of these latter probabilities. This will not prevent us from using the theorem, if we remember that in each case of applied probability we are obliged to accept a similar hypothesis concerning the equally probable cases; as, in spite of Kriess and other philosophers, there is no objective criterion for them. In both cases, if the obtained results conform, more or less, to those given by experience, our choice of the hypothesis will be more or less justified. No hypothesis can be proved by experience to be wrong in general, but only in particular cases. For example, the often debated Rule of Succession based on the hypothesis $\omega_i = \text{const.}$, can in certain

* Communicated by the Author.

cases be proved conformable to the results of experiment, in others adverse. Thus a contrary hypothesis, $\omega_i = \binom{n}{i} (\frac{1}{2})^n$, given by Boole and also by Stumpf, can be proved right or wrong, according to the case selected.

In this paper, an application of Bayes' theorem, for the inversion of Bernoulli's formula, will be made; though this use has often, quite unjustifiably, been contested. The fact that this inversion is generally stated in the textbooks in a very unsuitable way, has contributed to bring it into bad repute.

2. *Bernoulli's Theorem.* The probability p of the single event being given, the probability that among n observations there be ν favourable ones is expressed by

$$P_i = \binom{n}{\nu} p^\nu q^{n-\nu}, \dots \dots \dots (2)$$

where $q = 1 - p$.

Let us denote the ratio ν/n by $\bar{p}$; and let

$$\bar{p} - p = \frac{x}{n} \dots \dots \dots (3)$$

Substituting for ν in the formula (2) its value taken from (3) $\nu = x + np$, we have

$$P(x) = \binom{n}{x+np} p^{np+x} q^{nq-x} \dots \dots \dots (4)$$

For large values of n , this probability is given by the asymptotic formula

$$P(x) \sim \frac{k}{\sqrt{\pi}} e^{-k^2 x^2}, \dots \dots \dots (5)$$

where $k = 1/\sqrt{2pqn}$.

If p is known (4) and (5) express the probability that p satisfies (3).

Let us put in (5) $kx = t$, as according to (3) we have $\Delta x = 1$; therefore $\Delta t = k$; and it follows that

$$\Theta(\lambda k) = \frac{2}{\sqrt{\pi}} \int_0^{\lambda k} e^{-t^2} dt \dots \dots \dots (6)$$

is the probability that $\bar{p}$ satisfies the inequality (7),

$$|\bar{p} - p| < \frac{\lambda}{n} \dots \dots \dots (7)$$

3. *Inverse Problem.* The event having occurred ν times out of n , hence $\bar{p}$ is known; required the probability ΔW_i that the probability $p = p_i$ of the single event satisfies (3). If we accept an hypothesis concerning the *a priori* probabilities ω_i of p_i , the problem is solved by Bayes' theorem.

Let us admit that p_i may take indifferently one of the values $0, \frac{1}{m}, \frac{2}{m}, \dots, 1$. Therefore the probability *a priori* of $p_i = \frac{i}{m}$ will be $\omega_i = \frac{1}{m+1}$. And according to Bayes' theorem,

$$\Delta W_i = \frac{\frac{1}{m+1} \binom{n}{\nu} \left(\frac{i}{m}\right)^\nu \left(\frac{m-i}{m}\right)^{n-\nu}}{\sum \frac{1}{m+1} \binom{n}{\nu} \left(\frac{i}{m}\right)^\nu \left(\frac{m-i}{m}\right)^{n-\nu}}.$$

If S is the denominator of this expression, it is easy to show that

$$\lim_{m \rightarrow \infty} S = \frac{1}{n+1}.$$

ΔW_i will moreover satisfy (3) if

$$\bar{p} - \frac{i}{m} = \frac{x}{n}, \quad \dots \quad (8)$$

then the required probability will be

$$\Delta W_i = \frac{1}{S(m+1)} \binom{n}{\nu} \left(\bar{p} - \frac{x}{n}\right)^\nu \left(\bar{q} + \frac{x}{n}\right)^{n-\nu}, \quad \dots \quad (9)$$

where $\bar{q} = 1 - \bar{p}$.

And if m, n, ν , and $n - \nu$ are very large, the asymptotic value of this probability is

$$\Delta W_i = \frac{\bar{k}}{\sqrt{\pi}} e^{-\bar{k}^2 x^2} \Delta x, \quad \dots \quad (10)$$

where $\bar{k} = 1/\sqrt{2pqn}$; Δx is, according to (8), equal to $-\frac{n}{m}$.

Hence if $\bar{p}$ is known, (9) and (10) are expressions of the probability that p satisfies (3).

From (10) we conclude that if $\bar{p}$ is known the probability that p satisfies (7) is given by the same formula (6) as the solution of the corresponding direct problem, only $\bar{k}$ must be substituted for k .

The inverted theorem presented in this manner seems more acceptable than when given in the usual way*. If the interpreted problem is such that the hypothesis $\omega_i = \text{const.}$ is justified, the results proceeding from the use of this formula will be confirmed by experience.

January 1923.

LXXI. *The Fluorescence and Coloration of Glass produced by β -rays.* By J. R. CLARKE, M.Sc., F.Inst.P., Assistant Lecturer in Physics, The University, Sheffield†.

AT the 1922 meeting of the British Association, Mr. J. Ewles described some investigations into the fluorescence produced in various substances by cathode rays. He concluded that the fluorescence was due to a change in the state of molecular aggregation of the substances. Some observations on the coloration of glass by β -rays point to the same conclusion. Three specimens of glass tubing (of approximate composition 1.5 Na₂O, 0.5 CaO, 6 SiO₂; 1.4 Na₂O, 0.6 CaO, 6 SiO₂; 1.2 Na₂O, 0.8 CaO, 6 SiO₂; referred to as glasses 6, 7, and 9 respectively) were obtained from the Glass Department of this University, and kept in radium emanation, the supply of emanation being renewed from time to time till they were coloured a deep brown and ceased to fluoresce. Further radiation did not alter the colour. The walls of the tubing were about 1.5 mm. thick, but previous experiments with rods had shown that the coloration was due to β -rays, extending only to a depth to which these rays would penetrate. When the specimens were completely fatigued, each was divided into four, and a piece from each placed in an oven maintained at 110° C. They immediately began to fluoresce, and the time during which fluorescence persisted was noted. At the end of this time the glasses were decolorized. The other pieces were similarly heated to 180°, 235°, and 350°. The following results were obtained :—

Temperature.	Time of fluorescence in minutes.		
	Glass 6.	Glass 7.	Glass 9.
110°	13	13	13
180°	3	3	3
235°	1.25	1.25	1.5
350°	0.5	0.5	0.75

* See Czuber, 'Wahrscheinlichkeitsrechnung,' Third edition, 1914, vol. i. pp. 203-206.

† Communicated by the Author.

A piece of glass 9, also coloured, was heated to about 95°, and the fluorescence persisted for 15 hours. The intensity of the fluorescence was approximately inversely proportional to the time for which it persisted.

The conditions were such that the results are only approximate, but if curves be drawn showing the relation between the temperature and the time of fluorescence, they indicate, by extrapolation, that the glasses would be decolorized immediately if heated to a temperature between 500° and 600°, glass 9 requiring a slightly higher temperature than the others. The annealing temperatures of these glasses have been determined by Turner and English *, and found to be 526°, 538°, and 562° respectively. Tool and Valasek † have shown that there is an increased emission of heat when glass is cooled through the annealing temperature, indicating a change in the state of molecular aggregation at this temperature. Annealing proceeds at lower temperatures if the heating is sufficiently prolonged, and thus it is probable that if an unstable state of aggregation exists, it will slowly change to a stable state even when the temperature is low. The decoloration of the glasses, therefore, appears to be connected with a change in the state of molecular aggregation, coloration being the reverse process. As both coloration and decoloration were accompanied by fluorescence, it is probable that the fluorescence is due to this change.

It may be mentioned, further, that altogether nineteen different glasses have been radiated, fourteen of which were coloured brown and the remainder purple. I am indebted to my wife for chemical examination of these glasses. It was found that the five coloured purple all contained manganese, while the others did not. It has been stated frequently that soda-containing glasses are turned blue or purple by radiation. Varying amounts of soda were present in the glasses radiated, but the purple colour was not produced in the absence of manganese.

Sheffield,
January 26th, 1923.

* Journ. Soc. Glass Tech. iii. p. 125 (1919).

† Bureau of Standards Papers, No. 358 (1920).

LXXII. *Notes on X-ray Scattering and on J Radiations.*
By C. G. BARKLA, F.R.S., and RHODA R. C. SALE, M.A.,
University of Edinburgh.*

EARLY experiments by one of the writers on the transmission of Röntgen radiation through matter demonstrated the existence of secondary X-radiations of two and only two types—scattered X-radiation and fluorescent (characteristic) X-radiation. The former was not found to differ appreciably from the primary radiation exciting it, except in polarization, distribution, etc., the other was seen to be independent of the character (or wave-length) of the primary radiation.

The laws governing the emission of the scattered radiation were found to be of a very simple nature, and they led directly to the conclusion—a conclusion which has since been fully confirmed—that the scattering was produced by the electrons constituent in matter. One of these laws was that the intensity of scattering by *light* elements was independent of the penetrating power of the X-rays, *i. e.* the proportion of the energy of a beam lost by scattering during transmission through a thin layer of matter was independent (approximately) of the wave-length of the radiation used. Such a law, of course, had its limitations, and gave only the most important feature of the relationship—or lack of relationship—between scattering and quality of radiation. Whereas other properties of the rays varied enormously, the scattering was approximately constant during a variation of wave-length.

Later experiments† showed that when *heavy* elements were traversed by X-rays there was a considerable variation of scattering with wave-length, and that the heavier the element the greater in general was the rate of variation. It, of course, followed as highly probable that such variation existed when scattering was produced by light elements, though to a much less extent. It was also seen that the scattering by heavy elements approximated to equality with that by light elements mass for mass, when the wave-length was reduced. (It would probably be more accurate to say that the scattering per atom approximated to proportionality with the atomic number and not the atomic weight, though the experiments on heavy elements were not sufficiently extended to distinguish between the two.) The increase of scattering with the longer waves was explained as consequent

* Communicated by the Authors.

† Barkla and Miss Dunlop, *Phil. Mag.* March 1916.

upon the superposition in phase of effects from neighbouring electrons when the wave-length became comparable with the distances of the electrons apart.

In describing the later results, the variation of scattering with wave-length was not given absolutely, but by comparison with that in aluminium, a substance in which the variation was seen to be comparatively small.

There were several reasons why a further investigation of this variation seemed desirable. Absolute instead of comparative measurement, and greater accuracy were needed to furnish both a further test of the theory and to provide possible information regarding atomic structure.

In addition, it was seen that exact experiments would give valuable information on the question of a possible change in penetrating power in the process of scattering, and regarding the emission of a characteristic X-radiation of shorter wave-length than that of series K by elements of low atomic weight—such as had been strongly suggested by the experimental results of Barkla and Miss White*.

Regarding the former there has always appeared the possibility of a change in the properties of radiation produced by the process of scattering by electrons—particles of finite dimensions subject to restraining forces within the atom—or more probably still by groups of electrons where the relative dimensions are such as to make a group the scattering unit.

Though secondary X-radiations apparently differing considerably from the primary may very readily be obtained even when the lightest elements are used as scattering substances, we have never obtained convincing evidence of a change of quality of radiation *in the process of scattering*, except such as is given by polarization in the scattered radiation. One of our purposes was to look more closely for evidence of transformation—apart from the transformation (previously mentioned) occurring in the phenomenon of X-ray fluorescence, when characteristic radiations are emitted by the substance. The results of these preliminary researches are set down below. The investigation is being continued.

Variation of Scattering with Wave-length.

Barkla and Miss Dunlop† first showed the increase of scattering with wave-length in copper, silver, tin, and lead, by comparing the intensity of scattered radiation from

* Many of these are still unpublished. See Barkla, Bakerian Lecture, Phil. Trans. Roy. Soc. 1917; Barkla and White, Phil. Mag. Oct. 1917.

† Phil. Mag. March 1916.

such substances with the scattering from aluminium. The results are reproduced in Table I. They were corrected for absorption etc., and show relative intensities from equal masses of these elements when exposed to the same radiation.

TABLE I.

Showing relative intensities of scattered X-radiation of various wave-lengths from several metals.

X-radiation.		Scattering from Cu, Ag, Sn, and Pb compared with that from equal masses of Al.			
Approximate wave-length.	Approximate absorptability $(\mu/\rho)_{Al}$.	$\frac{(\sigma/\rho)_{Cu}}{(\sigma/\rho)_{Al}}$	$\frac{(\sigma/\rho)_{Ag}}{(\sigma/\rho)_{Al}}$	$\frac{(\sigma/\rho)_{Sn}}{(\sigma/\rho)_{Al}}$	$\frac{(\sigma/\rho)_{Pb}}{(\sigma/\rho)_{Al}}$
96×10^{-8} cm.	13	...	...	5.6	...
91 "	11	...	3.66	...	...
63 "	3.3	2.5	...	...	11.2
59 "	2.8	...	...	...	11.5
58.5 "	2.7	2.3	...	...	...
52 "	1.8	2.1	...	...	9.0
47 "	1.3	1.9	...	...	5.8
43 "	.95	1.5	...	...	4.4
38 "	.65	1.05?	...	...	2.85
316 "	.37	1.12	...	...	2.65
314 "	.36	1.07	1.37	...	2.1
311 "	.35	...	...	1.47	...
306 "	.33	...	1.25	...	1.9
305 "	.32	1.05	...	...	1.7

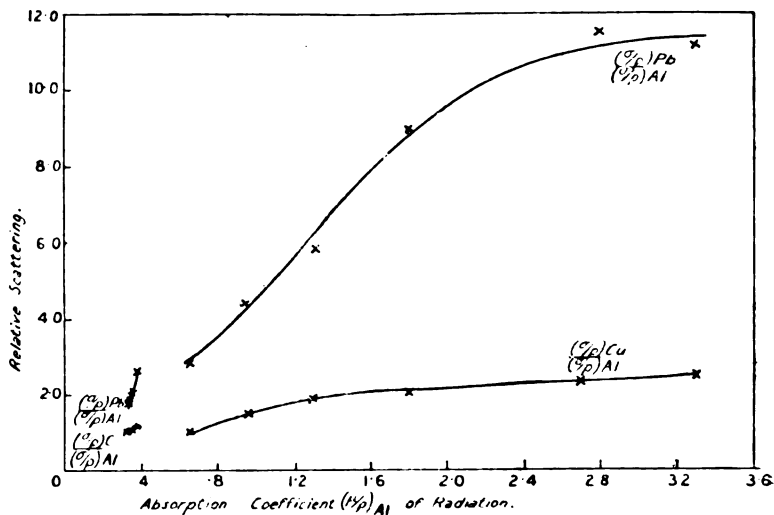
These indicate that the lighter the element the smaller is the variation of scattering with wave-length. Though the variation in aluminium itself was stated to be small, it was not given in the paper referred to.

Also within the range of wave-lengths employed, apparent discontinuities in the absorption curves for both copper and aluminium have more recently suggested the emission of J characteristic radiations (Barkla and Miss White)*. By plotting from Table I. "relative scattering" as obtained by Barkla and Miss Dunlop against absorption coefficient, it will be seen that an irregularity appears in the same region of wave-lengths as that in which discontinuities in absorption

* Phil. Mag. Oct. 1917.

were later found (fig. 1). No importance was attached to these when the scattering experiments were made—indeed, one of the values was queried because of its departure from the otherwise perfectly general law of increase of scattering with wave-length. The results were not examined till the whole series of observations was completed, and war work prevented a return to the experiments in search of the cause of the apparent irregularity.

Fig. 1.



[Recent examination of results of experiments upon which the conclusions shown in Table I. were based, shows that the irregularity was *largely* due to a step or discontinuity in the absorption curves, exactly as shown later in a paper by Barkla and White.]

We therefore determined to investigate more closely the scattering from copper, aluminium, and the lighter elements oxygen, carbon, and hydrogen (together) in filter paper. As in the previous investigations referred to, the homogeneous beams initially tried were not sufficiently intense for the measurements required, nor was the apparatus available for producing them. We used primary beams direct from the X-ray tube, and obtained the variation of wave-length by adjustment of gas pressure in the tube, the potential applied to the tube, and by filtering the radiation. Sheets of the above substances were placed in turn in the

primary radiation with the surface making an angle of 45° with the axis of the beam. The intensity of the scattered radiation proceeding in a direction at right angles to the primary radiation from the second face of the sheet was studied. In a comparison of the intensities of primary and secondary beams, errors due to absorption were thus avoided, or rather minimized, as both beams passed through the same thickness of radiator. The intensities of these two beams were measured by similar electroscopes placed in their path. The correction for scattering from air and all stray effects was found from similar observations taken in the absence of the radiating sheets.

From substances of higher atomic weight the scattered radiation or any possible characteristic radiation emerges only from a much smaller mass of radiating material owing to its greater absorbing power; hence the whole effect in the secondary electroscope is much smaller. More sensitive electroscopes in which the ionization was produced in sulphur dioxide were used to measure the scattered radiation, and two electroscopes were used in the primary beam for convenience in measuring the absorption coefficient of the radiation. The range of wave-lengths over which reliable readings could be obtained was, however, much shorter than in the experiments upon paper.

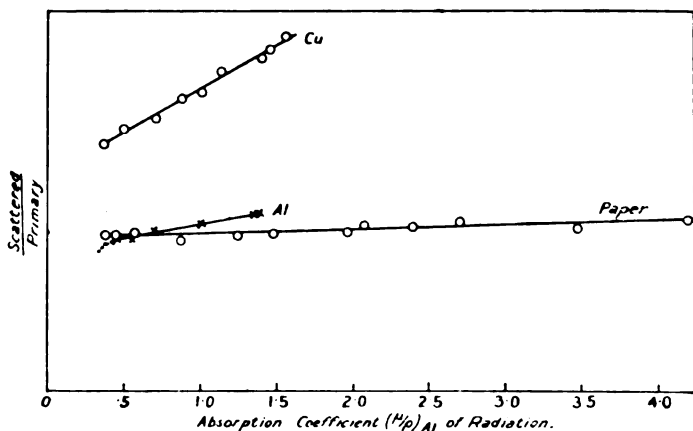
TABLE II.
Scattering from Paper.

Absorption Coeff. of Radiation (μ/ρ) _{Al} .	Observed Ratio of intensities, Secondary/Primary.	Stray effect.	Corrected Ratio of intensities, Secondary/Primary.
2.70	$\cdot 243 \times x$	$\cdot 022 \times x$	$\cdot 221 \times x$
2.41	$\cdot 235$	$\cdot 022$	$\cdot 213$
2.07	$\cdot 228$	$\cdot 013$	$\cdot 215$
1.48	$\cdot 228$	$\cdot 019$	$\cdot 209$
1.27	$\cdot 225$	$\cdot 019$	$\cdot 206$
0.87	$\cdot 221$	$\cdot 020$	$\cdot 201$
0.55	$\cdot 232$	$\cdot 025$	$\cdot 207$
0.44	$\cdot 233$	$\cdot 028$	$\cdot 205$
0.40	$\cdot 235$	$\cdot 032$	$\cdot 203$
4.20	$\cdot 243$	$\cdot 020$	$\cdot 223$
3.47	$\cdot 238$	$\cdot 022$	$\cdot 216$
1.97	$\cdot 235$	$\cdot 023$	$\cdot 212$

The results for paper are given in Table II., in which column 1 gives the absorption coefficient for the radiation,

column 2 the observed intensity of secondary radiation compared with intensity of the primary, and column 4 the corrected values after subtraction of the stray effect given in column 3. The corrected results are exhibited graphically in fig. 2, where the ratio of the intensities of the scattered and the primary radiations—so measured and in arbitrary units—is plotted against absorptivity of radiation (μ/ρ in Al). Over this range $\mu/\rho = \cdot 4$ to 4, the variation of scattering is very slight, but there is a small increase of scattering with wave-length amounting altogether to about 10 per cent. The increase cannot with certainty be distinguished from a linear one, though it is possible, indeed probable from other considerations, that the greater variation is at the two ends

Fig. 2.



of the range*. These results of experiments upon paper are of considerable interest for the emission of even a feeble characteristic X-radiation from one of the constituent elements, or a small rapid change in the scattering would have been apparent in the form of the curve (fig. 2).

There is no evidence here of the emission of a characteristic radiation or characteristic radiations from paper. The excitation of such a radiation in appreciable intensity would be apparent as a superposed fluorescent (characteristic) radiation for wave-lengths less than a certain critical value—i. e., passing from right to left of fig. 2, there would be a sudden rise in the curve for paper at a value for μ/ρ

* This was found in the case of aluminium at the high-frequency end, just beyond the limits of the observations given in this paper.

in Al of about $\cdot 8$, from Barkla and White's absorption experiments. There is no suggestion of this. It should, however, be pointed out that the rise to be expected from the absorption experiments is an exceedingly small one, for the change of absorption observed was not greater than a 15 per cent. rise, and in light elements only a small fraction of the energy absorbed has been found to be re-emitted as characteristic radiation (of series K). Thus a rise of an unknown but only a small fraction of 15 per cent. might reasonably be expected. As we could not be certain of detecting a variation of less than about 3 per cent., the evidence for or against it is not conclusive. The fraction of energy transformed into fluorescent (characteristic) radiation is, however, greater in elements of higher atomic weight; a characteristic radiation should therefore be more easily detected in these. From the experiments on aluminium it was evident there was a much greater change of scattering with wave-length. That this was not due to a superposed soft characteristic radiation, either from aluminium or from a small quantity of impurity (Fe) in the aluminium, was shown by placing sheets of aluminium in the paths of both primary and secondary beams. This absorbed the FeK radiation almost completely, yet a gradient of the same order of magnitude was found. The results are given in Table III. and plotted in fig. 2.

TABLE III.
Scattering from Aluminium.

Absorption Coefficient of Radiation (μ/ρ) _{Al} .	Ratio of Intensities, Secondary/Primary.
1.39	$\cdot 470 \times y$
1.35	$\cdot 465$
1.01	$\cdot 439$
$\cdot 69$	$\cdot 416$
$\cdot 56$	$\cdot 404$
$\cdot 463$	$\cdot 399$
$\cdot 46$	$\cdot 400$

In the experiments on the scattering from copper it was of course necessary, as in previous experiments, to eliminate the copper K radiation. This was effected by placing aluminium $\cdot 058$ cm. in thickness in the path of both primary and secondary beams after emergence from the radiator.

As shown in fig. 2 the variation of scattering from copper was found to be greater still than from aluminium. The same degree of accuracy cannot, however, be claimed for these readings, as a slight change of angle through absorption effects makes a considerable change in the slope or apparent variation of scattering with wave-length. Further experiments would need to be made to get the exact rate of variation: the results already obtained serve our immediate purpose.

As in the case of the paper there was no evidence either in the aluminium or copper curve of a discontinuity such as might have been expected to appear if characteristic radiation had been emitted. Thus these experiments give not the slightest evidence of the emission of a characteristic radiation of higher frequency than that of the K series.

As there was no appreciable characteristic X-radiation in any of these secondary beams, the radiations studied were presumably scattered X-radiations. Further evidence for this is, however, given below.

Any small transformation, unless constant in amount, might equally have been expected to show itself by a gradual change in the slope of the curves, for a change in absorptibility is accompanied by a change in ionizing power such as would have affected the measurements of the secondary radiation. This is not indicated in the curve for paper.

These results thus confirm the previous conclusions regarding relative rates of variation of scattering with wave-length obtained by direct comparison of various substances with aluminium. They also show with accuracy the small variation of scattering coefficient in the case of carbon, oxygen, and hydrogen, a greater variation in aluminium, and greater still in copper; in addition, they show the variation to be a gradual one over the range of wave-lengths employed.

Relative Intensities of Scattered Radiation from various Substances.

So far these experiments gave only rates of variation of scattering with wave-length of the radiation. Other experiments were undertaken to determine the relative intensities of the radiation scattered from equal masses of various substances.

In the experiments of Barkla and Miss Dunlop comparisons had been made between the scattering from various substances

with the scattering from aluminium. A more exact knowledge of the rate of variation of scattering with wave-length is obtained by comparison with the scattering from paper in which the variation is very small.

In these experiments two substances were compared directly. The thicknesses were adjusted so that the two radiating sheets absorbed the same proportion of the primary beam. As there were no marked selective effects over the wave-lengths employed, the correction for absorption was avoided. Thus a comparison was made of the scattering from the two radiators alternately placed in the same position in the primary beam. Dividing by the relative masses of the two we have the relative scattering by equal masses of the two substances. An absorbing sheet of aluminium was placed in the path of both the primary and secondary beams, and the ratio was found to be as nearly as measurable identical—showing the difference in intensity was not due to the superposition of soft characteristic radiation from any one of them. It showed too that if a change of absorbability was produced by re-emission (scattering), it was at least approximately the same for the radiation from paper, aluminium, and copper. For radiation of absorbability in aluminium (μ/ρ) equal to about 1.3, the relative intensities from aluminium and paper were found varying from 1.07 to 1.13, giving an average value of 1.1 (see Table IV.). In

TABLE IV.
Relative Scattering Al/Paper.

Absorption Coefficient μ/ρ in Al.	Thickness of Al before Electroscope.	Relative Scattering Al/Paper.
1.14	0 cm.	1.07
1.24	0	1.08
	.036	1.09
1.32	0	1.07
	.036	1.12
1.39	0	1.13
	.036	1.14
1.45	0	1.08

the experiments on the relative scattering from copper and aluminium, it was necessary, as in the previous experiments, to absorb the copper "K" radiation by placing aluminium .058 cm. in thickness before each electroscope; the radiation

scattered from aluminium was, of course, observed under identical conditions (see Table V.). The ratio of intensities

TABLE V.
Relative Scattering Cu/Al.

Absorption Coefficient μ/ρ in Al.	Thickness of Al before Electroscopes.	Relative Scattering Cu/Al.
·795	·204 ? cm.	1·73?
·858	·180	1·70
1·00	·180	1·88
1·22	·058	1·74
1·26	·056	1·88
1·26	·204	1·88
1·33	·058	1·86
1·5	·056	1·88

from copper and aluminium was very consistently about 1·87 when the absorbability of the radiation was approximately as before ($\frac{\mu}{\rho_{\text{Al}}} = 1·3$). This, again, agrees very well with the relative value 1·9 found by Barkla and Miss Dunlop by another method (see Table I.).

The results of these comparisons were then used to give the relative heights of the curves in fig. 2 by adjustment of the relative values for radiation of absorption coefficient = 1·3.

*Comparison of Absorption Coefficients of Primary
and Secondary Rays.*

As the experiments described furnished no evidence of the emission of a characteristic radiation of higher frequency than that of the K series, we proceeded to make a direct comparison of the penetrating powers of the primary and secondary X-radiations from light elements. In the earliest experiments by one of us*, when the conditions were made as simple as possible, and only moderately low frequencies were used, no difference in penetrating power of primary and scattered radiations could be found directly—yet some evidence of transformation was observed.

Later, differences were observed which appeared to indicate either the admixture of an unidentified fluorescent (characteristic) radiation, or just possibly a transformation in scattering.

* Phil. Mag. May 1903, June 1904.

These effects, however, were very variable in magnitude, and the further investigation of them was left for experiments of the kind described in the first part of this paper.

While the effect of variation of scattering with wave-length, and the emission of an X-radiation excited in the absorbing substance by the electrons constituting the secondary corpuscular radiation, must not be lost sight of, the principal source of uncertainty lies not in these but in the difficulty of obtaining a true measure of an intense primary beam of considerable cross-section. While it would be premature to give any decided opinion upon the nature of apparent transformations before the phenomena have been more fully investigated, our preliminary results sufficiently limit the possibilities to justify publication at this stage.

When thin sheets of paper were used as the scattering substance—in which case trouble due to differential absorption of primary and secondary beams in the radiating substance was avoided—experiments showed that the scattered was identical with the primary radiation throughout almost the whole range of wave-lengths experimented upon. This is seen from a comparison of the absorption coefficients of primary and secondary radiations, as given in Table VI., columns 1 and 2 respectively, and plotted in fig. 3. The simple law of equality where there is infinite possibility of variation is sufficient. Thus there is no doubt under certain conditions of an accurate equality of penetrating power of the scattered and primary radiations through a long range of wave-lengths included in these experiments, though this does not include the wave-length of the J absorption discontinuity of Barkla and White.

This conclusion is confirmed through a longer range of wave-lengths, in this case including the J absorption discontinuity, and without even the evidence of possible exception by the experiments on the variation of scattering with wave-length, the results of which are shown in fig. 2.

Thus under some conditions it is possible to obtain a secondary X-radiation from paper (O, C, and H) which is purely scattered radiation, without change in penetrating power and without admixture of fluorescent X-radiation, throughout the whole long range of wave-lengths. [The limits of experimental error are about 3 per cent. in intensity, or 3 per cent. in absorption coefficient.]

Under other conditions decided differences have been observed between the absorption coefficients of primary and secondary radiations, but only in the region of higher frequencies. This is shown by a comparison of the values

TABLE VI.

Absorption Coefficients (approximate) of Primary and Secondary Radiation (Scattered) from Paper.

Primary Radiation ($\mu \rho$ in Al).	Secondary Radiation ($\mu \rho$ in Al).	
Column (1).	Column (2).	Column (2x).
10.3	10.4	
8.46	8.76 (approx.)	
6.74	6.83	
6.39	6.51	
6.34	6.35	
6.23	6.32	
6.07	6.04	
6.03	6.16	
5.86	5.92	
5.73	5.72	
5.31	5.36	
5.18	5.12	
4.91	4.94	
4.88	4.85	
4.42	4.43	
3.27	3.20	
3.14	...	3.45
2.46	...	2.90
2.33	...	2.83
2.07	2.18	
2.05	2.14	
1.90	2.00	
1.83	...	2.02
1.51	...	1.94
1.47	...	1.83
1.16	1.21	
1.15	1.20	
0.65	...	0.90?
0.58	...	0.82?
0.54	...	0.70?

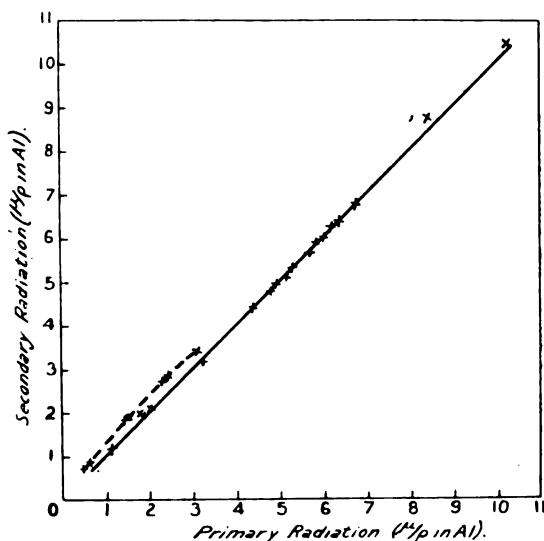
in columns 1 and 2x, obtained at other times with the same experimental arrangement. The corresponding points are connected by the broken line of fig. 3. It is important to notice that if such transformations had occurred during the experiments on the variation of scattering with wave-length we might have expected quite a large deviation from the simple relationship shown in fig. 2, in the curve for paper, for a change in absorbability normally implies a change in ionizing

power which would have been detected in the ionization produced in the secondary electroscope.

This fact compels us to consider very critically the transformations which have been observed in many experiments and have recently been recorded by Crowther and by A. H. Compton.

It should also be observed that no step in the absorption curve for paper has ever been found of anything like the magnitude required to explain Crowther's results.

Fig. 3.



Thus, if appreciable transformation does occur, it is only under special conditions which have not yet been identified. Moreover, we quite realise that experiments indicating such transformation have not been made under conditions which entirely eliminate the possibility of error or of an explanation in terms of certain phenomena observed in our experiments upon the J absorption discontinuities. The transformed radiations, if true transformation in the paper be established, are not subject to the same laws as those governing the fluorescent radiations of series K, L, and M.

We shall, however, have more to say concerning the J_2 radiations.

Summary.

Further experiments on the scattering of X-rays show that even the light elements hydrogen, carbon, and oxygen (together) show a very slight increase of scattering with wave-length. Over a considerable range, however, the outstanding feature is the constancy of the scattering coefficient—as compared with absorption and other coefficients.

In aluminium, and more markedly in copper, the scattering increases more rapidly with wave-length.

The relative intensities of scattering by hydrogen, carbon, and oxygen (in paper), aluminium, and copper have been obtained by another method, and the results for the last two—the others have not been previously determined—agree very closely with those given by Barkla and Miss Dunlop.

Over a considerable range of wave-lengths no difference between the absorption coefficient of the primary radiation and of the secondary X-radiation (scattered) from paper has been detected. The marked differences sometimes appearing when the higher frequency radiations are used have not been observed under conditions justifying any definite conclusion regarding their origin. Further experiments are, however, being conducted, as the investigation does not appear to have completely exhausted all possibilities of an explanation in terms of the simple laws of scattering, fluorescence, and absorption, which have already found general acceptance.

These investigations have not furnished the evidence of the existence of J characteristic radiation which so many results led us to expect. Further communications on this subject will, however, shortly be made.

LXXIII. *Some Properties of Resonance Radiation and Excited Atoms.* By K. T. COMPTON, Ph.D., Professor of Physics, Princeton University*.

IN accounting for spectral lines, for their variation in intensity with different conditions of excitation and for phenomena of cumulative ionization, attention has recently been drawn to the existence of atoms and molecules in various conditions of partial or complete ionization. In particular, that type of excited atom which results from the first displacement of an electron from its most stable position

* Communicated by the Author.

is of great interest because it may be produced in such quantity, by proper excitation, as to give to the gas properties which are quite different from those of the normal unexcited gas. Such properties include the appearance of new lines in the absorption spectrum, new types of resonance radiation, band spectra associated with molecular combinations between excited atoms and increased ease of ionization. A study of these properties has led to discoveries of importance in the theories of atomic structure and of radiation.

In recent papers * the writer discussed the two ways in which atoms may be put into the excited, or partially ionized, state. It was shown that, in a discharge-tube, the number of atoms in the excited state as a result of a preceding electronic impact is exceedingly small in comparison with the number in this state through absorption of the resonance radiation excited by electronic impacts against neighbouring atoms, unless the gas pressure is very low. This fact suggests an interpretation of experiments of Franck and Knipping † and of Kannenstine ‡ on metastable helium.

The conception of partial ionization by resonance radiation is as follows :—When an electron whose velocity exceeds that gained by falling through the resonance potential V_r collides with an atom, it displaces an electron from the normal to the next outer orbit, making an excited atom. After a time-interval, of average duration τ , this electron falls back to its original position and emits a quantum $h\nu$ of resonance radiation. Any other normal atom is capable of absorbing this radiation, and re-emitting it after an average interval τ . The radiation is thus passed on from atom to atom, putting one after another into the excited state, until it finally escapes from the gas or is degraded into light of lower frequency as a result of a temporary chemical combination made by an atom while in the excited state.

Formally, if not physically, the passage of resonance radiation through a gas may be treated as a problem in diffusion ; for the intensity of a beam of light is reduced by absorption or resonance scattering according to the equation $I=I_0e^{-\alpha x}$, and the number of molecules passing through a gas in a parallel beam falls off according to the similar equation $N=N_0e^{-x/t}$. Thus the reciprocal $1/\alpha$ of the absorption coefficient is analogous to the mean free

* Phys. Rev. xx. (1922); Phil. Mag. xliii. p. 531 (1922).

† *Zeit. f. Phys.* i. p. 320 (1920).

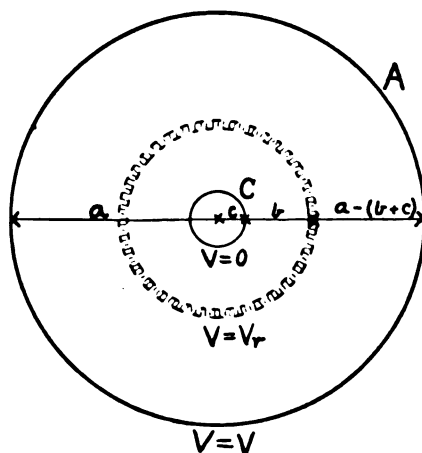
‡ *Astrophys. Journ.* lv. p. 345 (1922).

path l . It follows that the average speed with which a quantum of radiant energy moves through a gas equals $\frac{l}{\alpha\tau}$, or its mean free path l/α divided by the average time τ during which it is absorbed by the atom at the end of its path. Thus we may apply the diffusion equation from the Kinetic Theory of Gases, and put

$$\iint \frac{1}{3} \frac{1}{\alpha} \frac{1}{\alpha\tau} \frac{dN'}{dn} dS = - \iiint R dx dy dz, \quad . \quad . \quad (1)$$

in which N' is the number of excited atoms per unit volume at any point, n is the outward normal to the element of surface dS , and R is the rate of production of new quanta

Fig. 1.



per unit volume. The surface integral gives the rate of "diffusion" of quanta across the closed surface, and the volume integral gives the rate of production within it. By applying this equation we can calculate the concentration N' of excited atoms at any point in the gas, as is done for coaxial cylindrical electrodes in the following treatment.

Electrons from the hot cathode C collide inelastically with atoms, giving rise to resonance radiation, in the shaded layer. If the length f of the electrodes is large compared with the distance $(a - c)$ between them, this resonance radiation diffuses only inward and outward, ultimately being absorbed by the electrodes.

If n electrons per second leave the cathode, and if P is

the fraction of atoms in the excited state in the shaded layer, then $n(1-P)$ is the number of quanta of resonance radiation produced in this layer per second. $n_a(1-P)$ quanta diffuse outward to the anode and $n_c(1-P)$ diffuse in toward the cathode. If we apply equation (1) to a cylindrical surface of radius r , lying outside the shaded layer, we have

$$\frac{1}{3\alpha^2\tau} \frac{dN'}{dr} (2\pi r f) = -n_a(1-P);$$

whence

$$N'_a = - \frac{3\alpha^2\tau n_a(1-P)}{2\pi f} \log r + C_a$$

is the value of N' at any point outside the shaded layer. If the reflecting power of the anode for resonance radiation is negligibly small, $N'_a=0$ when $r=a$, whence

$$N'_a = \frac{3\alpha^2\tau n_a(1-P)}{2\pi f} \log \frac{a}{r}.$$

Similarly, at points inside the neutral surface,

$$N'_c = \frac{3\alpha^2\tau n_c(1-P)}{2\pi f} \log \frac{r}{c}.$$

But $n_a+n_c=n$ and at the layer $r=(b+c)$ we have $N'_a=N'_c=N'$. It is thus easily shown that

$$N'_a = \frac{3\alpha^2\tau n(1-P)}{2\pi f} \frac{\log \frac{b+c}{c}}{\log \frac{a}{c}} \log \frac{a}{r},$$

$$N'_c = \frac{3\alpha^2\tau n(1-P)}{2\pi f} \frac{\log \frac{a}{b+c}}{\log \frac{a}{c}} \log \frac{r}{c}.$$

Integrating N'_a over the volume of gas outside the shaded layer and N'_c over the volume within it, and adding, we obtain

$$N = \frac{3\alpha^2\tau n(1-P)}{4 \log \frac{a}{c}} \left\{ [a^2 - (b+c)^2] \log \frac{b+c}{c} - [(b+c)^2 - c^2] \log \frac{a}{b+c} \right\} \quad (2)$$

as the total number of excited atoms between the electrodes in the gas.

Phil. Mag. S. 6. Vol. 45. No. 268. April 1923. 3 C

In deriving this expression, we assumed that the reflecting power of the electrodes for resonance radiation is negligible. If we had included it in our calculations, the constant C_a would have taken a more complicated value and the value of N in equation (2) would have been increased. The error thus introduced is relatively small, however, especially for resonance radiation of short wave-lengths.

In equation (2) a and c are dimensions of the apparatus, and b depends on the distribution of potential between the electrodes. The fraction P of atoms in the excited state at the shaded layer is usually small compared with unity*, although it is possible that it may approach unity in very intense arcs. τ is the average interval between absorption and emission of a resonance quantum of energy by an atom. According to classical dynamics this is the reciprocal of the electromagnetic damping constant, or

$$\tau = \frac{3mc^3}{8\pi^2 e^2 \nu^2}, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where e and m are the electronic charge and mass, c is the velocity of light, and ν is the frequency. From this we calculate $\tau = 2(10)^{-8}$ sec. for the H_a line. For the resonance radiation in helium we calculate $\tau = 1.7(10)^{-10}$ sec. The most accurate experimental determinations of τ are probably those of Wien†, who found $\tau = 2.35(10)^{-8}$ sec. for H_β and H_γ , and about the same value for lines and bands of oxygen and nitrogen. These are of the order of magnitude to be expected from equation (3), but do not accurately confirm it, since very little variation of τ with frequency ν was found. The direct experimental data are meagre, and give no information as to whether τ is the same for resonance as for other radiation, or whether the approximate agreement with equation (3) in the region of the visible spectrum is a mere coincidence.

The scattering coefficient α is very difficult to measure, since it is only the central monochromatic portion of a resonance line which is scattered by the gas. Lamb‡ gives a very general law of resonance scattering, applicable if every molecule possesses an oscillator of resonance frequency. Under this condition his law may be expressed in the form

$$\frac{p}{\alpha} = \frac{1.54}{N\lambda^2}, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

* K. T. Compton, *loc. cit.*

† *Ann. d. Phys.* lx. p. 597 (1919), p. 229 (1921); also Dempster, *Phys. Rev.* xv. p. 138 (1920).

‡ *Camb. Phil. Soc. Trans.* xviii. Stokes Commemoration (1900).

where p is the pressure in millimetres, N is the number of scattering atoms per cm.^3 at 1 mm. pressure, and λ is the wave-length of the resonance radiation. Equation (4) gives a theoretical upper limit for α . This limit might be approached if there were entire absence of Doppler shifts, and if every atom were at every instant possessed of an oscillator capable of responding to resonance frequency.

Actually α has not been measured for any resonance line except mercury 2536, owing to experimental difficulties. For this line Wood's results* yield a value $p/\alpha = 6.75(10)^{-4}$ cm. as the "mean free path" of the resonance radiation at 1 mm. pressure. Equation (4) gives a value $6.6(10)^{-8}$ cm., about 10,000 times smaller than the observed value, assuming every atom to be effective in scattering. This discrepancy must be due (1) to inability to get strictly monochromatic light, (2) to the Doppler effect of the moving atoms, and (3) to the fact that an atom probably has the internal configuration to permit its absorption of a given frequency only at repeated intervals. For helium, equation (4) gives $p/\alpha = 1.16(10)^{-6}$ cm.

It is evident that our present knowledge of α and τ is insufficient to permit the use of equation (2) for anything but the very roughest estimates of the number N of excited atoms to be expected in an apparatus on the present theory. Nevertheless, some interesting suggestions can be made.

Kannenstine† found, by use of an alternating voltage of variable frequency to produce an arc by thermionic bombardment in helium, that excited helium atoms could be detected as long as 0.0024 sec. after the exciting voltage had been removed. If excited atoms are produced only, or mainly, as a direct result of electron impacts, then 0.0024 sec. must be time during which *individual atoms* persist in the excited state. It must be, approximately, the value of τ , and therefore about 100,000 times larger than any value of τ measured directly and 15,000,000 times the classical value predicted by equation (3).

If, on the other hand, excited atoms may also be formed by absorption of resonance radiation, the interpretation of Kannenstine's work is quite different and more in harmony with our other evidence. 0.0024 sec. represents the time required for the resonance radiation to escape from the gas, by the mechanism discussed in this paper, and this may include the time of many thousands of absorptions and re-emissions. An accurate solution of the relation between

* 'Recent Researches in Physical Optics.'

† *Loc. cit.*

0.0024 sec. and τ may be obtained by a Fourier series method, analogous to that used for the escape of heat from a cylinder whose initial distribution of temperature is given. The following simpler method is sufficiently accurate for the present purpose.

At the instant the voltage is shut off, $n(1-P)$ is the rate of production of new quanta, and hence the rate of escape of quanta from the gas, and equation (2) gives the total number of quanta N in it. Hence $N/10n(1-P)$ is the number of seconds t' required for 1/10 of the quanta to escape from the gas, if the loss were to continue at the initial rate during this interval, which is not quite true. If we neglect this relatively small error, and substitute for N from equation (2), we have

$$t' = \frac{3\alpha^2\tau}{40 \log_c a} \left\{ [a^2 - (b+c)^2] \log_c \frac{b+c}{c} - [(b+c)^2 - c^2] \log_c \frac{a}{b+c} \right\}. \quad (5)$$

The true value of t' must be a little greater than this.

It is difficult to estimate the ratio by which the number of excited atoms decreased during the time 0.0024 sec. in Kannenstine's experiments. He would certainly have detected as many as 1/10 the initial number, and would probably not have detected them if reduced to 1/1000. These reductions correspond approximately to time intervals of $22t'$ and $66t'$, respectively. Probably about 1/100 of the initial number would have been detected, corresponding to about $44t'$. This is, then, the quantity to which his time of 0.0024 sec. refers. We may, therefore, to at least the right order of magnitude, put

$$0.0024 = \frac{33\alpha^2\tau}{10 \log_c a} \left\{ [a^2 - (b+c)^2] \log_c \frac{b+c}{c} - [(b+c)^2 - c^2] \log_c \frac{a}{b+c} \right\}. \quad (6)$$

From this equation, τ could be found if α were known, and *vice versa*.

In an ordinary arc, stimulated by electronic bombardment, we may take $a=1$ cm., $c=0.02$ cm. as approximate dimensions of the apparatus. In the arc, with a positive space-charge around the cathode, b appears to be of the order of the electronic mean free path in the gas*, and hence about 0.1 cm. in Kannenstine's experiments. This

* Compton, Phys. Rev. (in print).

makes the term in braces in equation (6) equal to about 1.8, and any reasonable values of a , b , and c lead to this order of magnitude. We have, then,

$$\alpha^2\tau = 0.0016 \quad . \quad . \quad . \quad . \quad . \quad (7)$$

as a rough expression of the relation between α and τ given by Kannenstine's experiments.

If we assign to α the upper limiting value, as given by equation (4), we find $\tau = 2.2(10)^{-15}$ sec. If we suppose that c is actually about 10,000 times smaller than the limiting value for helium, as it appears to be for mercury, we have $\tau = 2.2(10)^{-7}$ sec. If we assume that the resonance radiation is scattered at the same rate in helium as in mercury, we have $\tau = 0.75(10)^{-9}$ sec. Owing to its simple structure, we should expect a larger proportion of helium than of mercury atoms to be in a condition capable of absorbing resonance radiation at any instant, so that we should expect the estimate $\tau = 2.2(10)^{-7}$ sec. to be too large. *The most reasonable interpretation of Kannenstine's experiments would seem, therefore, to indicate a value of τ for helium which is not noticeably larger than for other substances.*

Unsatisfactory as this treatment is, owing to uncertainty regarding the value of α , it at least serves to emphasize the tendency of resonance radiation to remain imprisoned within a gas for a time which may be enormous in comparison with the time τ of imprisonment within individual atoms. α is proportional to the gas pressure, so that this imprisoning effect should become more important at high pressures, and become negligible below pressures at which the mean free path of the radiation $1/\alpha$ exceeds the dimensions of the apparatus. We should expect Kannenstine's time-interval 0.0024 sec. to increase with increasing gas pressure, although this would be partially masked by the accompanying decrease in b and, possibly, by change in the space-charge conditions. He states that the persistence of metastable atoms was more marked at higher than at lower pressures, although no noticeable difference in time of persistence was found.

The general idea embodied in the above treatment appears to be a necessary consequence of the nature of resonance radiation. May the resonance radiation disappear from the gas in any other manner than by diffusion out of its boundaries as discussed above? It seems certain that the resonance radiation may be "degraded" into radiation of other wave-lengths during the existence of temporary compounds with other atoms of the same, or of different gases.

Thus increase of pressure, or addition of relatively chemically active impurities, would tend to diminish the amount of resonance radiation imprisoned in the gas and, therefore, the number of excited atoms. Several facts may be accounted for by such "degradation."

Lyman * reports spectroscopic observation of helium lines 584.4, 537.1, 522.3, and 515.7 Å, which seem to be the lines of the principal singlet series $0S-mP$. If this be true, the line 584.4, which corresponds to the 21.2 volt resonance potential, does not represent a transition in violation of the selective principle, and there is therefore no theoretical reason for believing the corresponding type of excited atom to have an abnormally long life τ . Lyman also reports a queer diffuse line at 600.5 Å, corresponding to the 20.4 volt resonance potential, which is usually a stronger effect than that at 21.2 volts, and possesses stronger resonance properties. The spectroscopic character of this line would be accounted for if atoms in the 20.4 volt excited state are chemically more active than in the 21.2 volt state, resulting in the formation of temporary helium compounds. The internal forces, or the alterations in the internal energy, would alter the frequency of the radiation emitted when the atoms return to the normal state, so that this would not be resonance radiation. Since the helium compounds are very unstable, such an effect would result in a distributing of the original resonance radiation into a not very wide diffuse line or band as observed. There is independent evidence that the 20.4 volt excited atoms are chemically active †. In addition to such a diffuse line, a regular band spectrum, to which the energy of the absorbed resonance radiation might conceivably contribute, would be expected from the helium molecules—as is the case ‡.

In the presence of other gases, any of which would be chemically more active and would be photoelectrically ionized by the resonance radiation of helium, this radiation would be converted into other and longer wave-lengths more rapidly than in pure helium, both through excitation of the line spectra of impurities and band spectra of various temporary molecular combinations. This suggests an explanation of results of Franck and Knipping, who found the photoelectric effect of 20.4 volt resonance radiation to become relatively weaker as the helium was purified, and interpreted this as indicating that the return of such metastable atoms

* Science, lvi. p. 167 (1922).

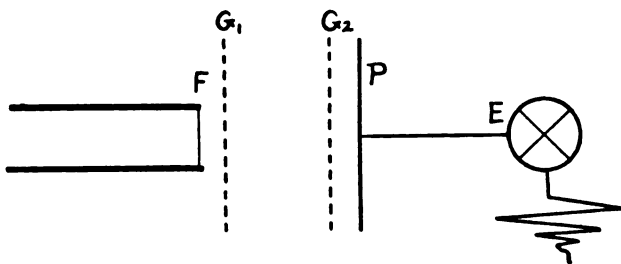
† Francke & Reiche, *Zeit. f. Phys.* l. p. 154 (1920).

‡ Curtiss, Roy. Soc. Proc. A, ci. p. 38 (1922).

to the normal state occurred only in the presence of foreign gas molecules.

Their apparatus was of the familiar type indicated in fig. 2, the radiation resulting from electron impacts with molecules between two gauzes G_1 and G_2 , and being detected by the photoelectric effect on the plate P. If the radiation is strictly of the resonance type, it would tend to be absorbed in the gauzes, owing to the extremely short "mean free path" of the radiation. It is as if the wire of the gauze were a perfect absorber of molecules introduced between the gauzes and allowed to diffuse outward with a very short free path through the helium. Relatively few would reach the plate P. In the presence of impurities, on the other hand,

Fig. 2.



the resonance radiation would be transformed into non-resonance wave-lengths, and would pass freely through the openings in the gauze and produce a photoelectric effect on the plate P.

It may be suggested, furthermore, that "degradation of resonance radiation," in some such manner as is here suggested, seems necessary to account for the tendency of radiation to become adapted, as regards spectral distribution of energy, to the temperature of the medium through which it is passing. Without such degradation, the observed radiation from the sun would be more characteristic of its hot interior than is actually the case.

Conclusion.

The present discussion, though rather speculative and dealing with quantities which are very uncertainly known, yet serves to point out certain important properties of resonance radiation, and calls attention to the bearing which these may have on the very important but elusive problem of the existence of atoms in various excited states.

It is shown (1) that the passage of resonance radiation through a gas may be treated as a problem in diffusion, (2) that the number and persistence of excited atoms depends jointly on the average time of activation τ of an atom and the square of the scattering coefficient α^2 of the resonance radiation in the gas and may be calculated, and (3) that the presence of impurities may affect experiments on the properties of resonance radiation by causing its transformation into other wave-lengths to which the gas is more transparent.

Note added with proof.—Attention is called to a paper on this subject, by F. A. Horton and A(nn) C. Davies (Phil. Mag. xliv. p. 1140, 1922), in which conclusions similar to those in this paper are reached.

Palmer Physical Laboratory,
Princeton, New Jersey, U.S.A.

LXXIV. *Testing the Expressions for the Longitudinal and Transverse Masses of the Electron.* By L. T. JONES and W. C. POMEROY*.

SINCE the first work of Kaufmann† demonstrating the mass of the electron to be a function of the velocity, a very considerable amount of experimental labour has been performed by various investigators‡ to verify the law of variation. In each case the method has involved only the transverse mass, and the curves representing the various theories lie so close together that it is difficult to decide which is most nearly correct.

The first suggestion of an experimental method involving the longitudinal mass was made by Einstein§. The difficulties of the method are obviously great and no one has carried it out.

Page|| has derived an equation relating to Hull's magnetron¶ and involving the relativity expressions for both

* Communicated by the Authors.

† *Gesell. Wiss. Gott. Nachr.* iii. pp. 90-103.

‡ Neumann, *Ann. d. Phys.* xlv. p. 529; Guye and Ratnosky, *Arch. des Sci.* xxxi. p. 293; Guye and Lavanchy, *Arch. des Sci.* xlii. pp. 286, 353, 441; Jones, *Phys. Rev.* viii. p. 52; Bucherer, *Ann. d. Phys.* xxx. p. 974; and others.

§ Einstein, *Ann. d. Phys.* xxxi. p. 583.

|| Page, *Phys. Rev.* xviii. p. 58.

¶ Hull, *Phys. Rev.* xviii. p. 31.

masses. This equation lends itself to experimental verification, though the labour necessary is great.

The equations derived in the following pages are based on an experimental method by which the expressions for the longitudinal and transverse masses of the electron may be verified, not only for the Lorentz-Einstein electron, but for those of Abraham, Walker, and Bucherer-Langevin as well. The calculated curves of fig. 2, representing the several theories, are seen to lie twice as far apart as those encountered in previous investigations, where only the transverse mass was involved.

The Method.

The essential portions of the apparatus (fig. 1) are enclosed in a vacuum maintained as high as possible. A battery heats the filament of the cathode, C. The anode, A, is

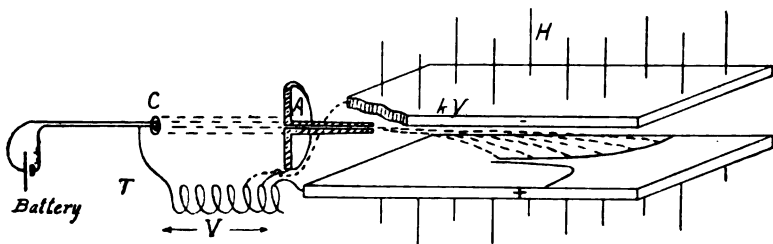


Fig. 1.

provided with a tube of small bore for the purpose of restricting the beam. This tube terminates midway between the two brass plates, which are horizontal. By means of the transformer, T, a high alternating potential is maintained between the cathode and anode, while a small fraction, k , of this discharge-voltage is maintained between the horizontal brass plates. The electrostatic field between these plates is thus variable and in phase with the discharge-voltage. Distortion of the field is eliminated by having the anode potential midway between the potentials of the two plates. In the discharge-chamber each electron undergoes an acceleration along the axis of the tube. When it passes through the anode and enters the deflexion-chamber it is accelerated downward by the electric field between the two plates. The total time of travel of any one electron is small compared with the time of alternation of the discharge-voltage.

A constant magnetic field, H , collinear with the electrostatic field deflects the electron beam to one side or the other of the centre line. The dotted lines indicate the electron paths when a large number of velocities are present. The more rapidly moving electrons have the shorter range. The electron beam leaves its trace on a photographic film deposited on the lower of the two horizontal brass plates. When no magnetic field is present this trace is a straight line down the centre of the plate. The two directions of the magnetic field will give two curves, one on either side of the centre line. The form of these curves will be compared with those calculated by the various theories.

The Calculation of the Curves.

Let

- v = velocity of the electron,
- β = the usual velocity ratio,
- m_t = transverse mass of the electron,
- m_l = longitudinal mass,
- V = instantaneous value of discharge-voltage, e.m.u.,
- e = charge of the electron,
- c = velocity of light.

The work done by the discharge-voltage in carrying the electron from cathode to anode is

$$Ve = \int m_l v \, dv,$$

whence

$$Ve = \int_0^\beta m_l v^2 \beta \, d\beta. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The Action of the Electrostatic Deflecting Field.

Since the electron experiences no appreciable change in velocity while traversing the deflexion chamber, the transverse and longitudinal masses may be considered constant during that interval, having the values corresponding to its particular velocity. The horizontal velocity and the vertical acceleration are thus constant in this region.

The downward force of the electrostatic field on the electron is

$$\frac{kVe}{2d} = m_t a, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

- where kV = instantaneous voltage between plates,
- $2d$ = distance between the two plates,
- a = the acceleration of the electron.

Since the electron enters midway between the two plates, the distance of fall is

$$d = \frac{1}{2}at^2, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and the range is

$$R = vt = c\beta t, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where t is the time of travel from anode to film.

From equations (2), (3), and (4) we have

$$Ve = \frac{4m_e d^2 c^2 \beta^2}{kR^2} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The Action of the Magnetic Field.

During the passage of the electron through the electrostatic field it is also subject to the action of a uniform and constant magnetic field, H . Its path is bent, in the horizontal plane, into a circle of radius r . The force of the magnetic field on the electron is

$$Hev = \frac{m_e v^2}{r} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

If the deflexion, y , due to the magnetic field is small, it is represented with sufficient accuracy by

$$y = \frac{R^2}{2r} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

From equations (6) and (7), placing $v = c\beta$, we obtain

$$He = \frac{2m_e y c \beta}{R^2} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

In equations (1), (5), and (8) the various expressions for m_e and m_t are to be introduced, yielding expressions for the coordinates R and y .

The Lorentz-Einstein Theory.

The Lorentz-Einstein * expressions for the two masses are

$$m = m_0(1 - \beta^2)^{-1/2},$$

$$m = m_0(1 - \beta^2)^{-3/2}.$$

* H. A. Lorentz, 'Theory of Electrons.'

Substituting in equation (1)

$$Ve = \int_0^\beta m_0 c^2 (1 - \beta^2)^{-3/2} \beta d\beta \\ = \left[m_0 c^2 (1 - \beta^2)^{-1/2} \right]_0^\beta,$$

or $Ve = c^2(m_t - m_0). \quad \dots \dots \dots (9)$

Combining equations (5) and (9)

$$c^2(m_t - m_0) = \frac{4m_e d^2 c^2 \beta^2}{kR^2}.$$

Replacing m_t by $m_0(1 - \beta^2)^{-1/2}$ we have

$$R^2 = \frac{4d^2 \beta^2 (1 - \beta^2)^{-1/2}}{k[(1 - \beta^2)^{-1/2} - 1]} \dots \dots \dots (10)$$

From (8)

$$y = 2H \frac{e}{m_0} \frac{d^2}{ck} \frac{\beta}{[(1 - \beta^2)^{-1/2} - 1]} \dots \dots \dots (11)$$

Elimination of β by (10) and (11) yields the equation of the trace on the photographic film :

$$y = \frac{H \frac{e}{m_0} R^2 \left[1 - \frac{4d^2}{kR^2} \right]}{2c \sqrt{\frac{8d^2 - kR^2}{kR^2}}} \dots \dots \dots (12)$$

This may also be written

$$\frac{e}{m_0} = \frac{2cy \sqrt{\frac{8d^2 - kR^2}{kR^2}}}{HR^2 \left[1 - \frac{4d^2}{kR^2} \right]} \dots \dots \dots (13)$$

Experimental values placed in the right member should give a constant and correct value for e/m_0 if the Lorentz-Einstein expressions for the two masses be correct. Since the expression for m_t has already been subjected to frequent test and has been verified repeatedly, this may be considered a rigid test of their expression for m_t .

The apparatus at present being used to carry out this method permits use of the following constants :—

$$\begin{array}{ll} k = \cdot 01. & H = 3\cdot 5 \text{ gauss.} \\ d = 1 \text{ cm.} & e/m_0 = 1\cdot 765 \times 10^7. \\ c = 3 \times 10^{10}. & \end{array}$$

Assuming values of β we may calculate the corresponding values of the coordinates R and y by the use of (10) and (11). These values are given in columns 2 and 6 of Table I. The curve plotted from these values is indicated in fig. 2.

TABLE I.

R cm.					y cm.			
	Lorentz-Einstein.	Abraham.	Bucherer-Langevin.	Walker.	Lorentz-Einstein.	Abraham.	Bucherer-Langevin.	Walker.
1	28.24	28.16	28.27	28.26	8.17	8.17	8.22	8.20
2	28.14	28.07	28.18	28.21	3.994	3.99	4.04	4.02
3	27.96	27.90	28.06	28.11	2.559	2.60	2.63	2.59
4	27.69	27.81	27.88	27.96	1.809	1.87	1.85	1.84
5	27.31	27.51	27.62	27.75	1.331	1.40	1.43	1.37
6	26.83	27.15	27.27	27.47	.988	1.066	1.10	1.03
7	26.19	26.62	26.78	27.08	.720	.806	.844	.766
8	25.30	25.91	26.07	26.51	.494	.590	.623	.539
9	23.96	24.83	24.93	25.61	.286	.390	.410	.324

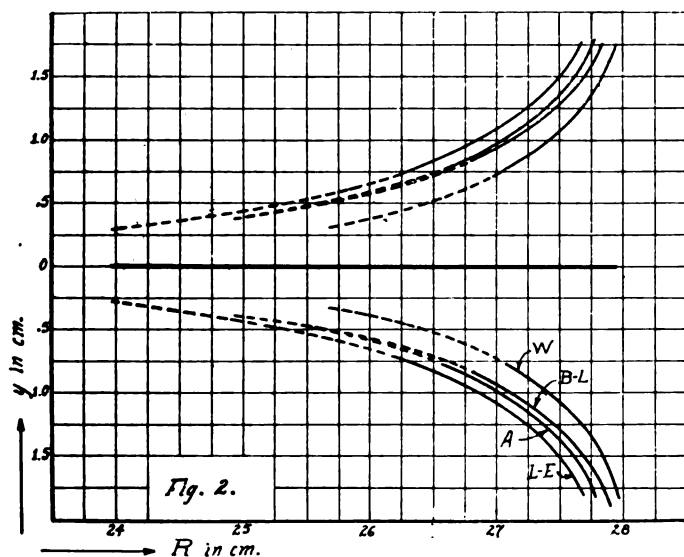
$$d = 1 \text{ cm.}$$

$$k = .01.$$

$$H = 3.5 \text{ gauss.}$$

$$e/m_0 = 1.765 \times 10^7.$$

$$c = 3 \times 10^{10} \text{ cm./sec.}$$



In meeting certain objections that have been raised to Lorentz's derivation of the mass expressions, Walker* has derived values which, as corrected by Schott†, are :

$$m_t = m_0(1 + \frac{1}{6}\beta^2)(1 - \beta^2)^{-1/2},$$

$$m_l = m_0(1 - \frac{1}{3}\beta^2)(1 - \beta^2)^{-3/2}.$$

Substituting this value of m_l in equation (1) we have

$$Ve = \int_0^\beta m_0 c^2 (1 - \frac{1}{3}\beta^2)(1 - \beta^2)^{-3/2} \beta d\beta. \quad (14)$$

Integrating by parts this becomes

$$Ve = \frac{2}{3} m_0 c^2 [(1 - \beta^2)^{-1/2} (1 + \frac{1}{3}\beta^2) - 1]. \quad (15)$$

Placing Walker's expression for m_l in equation (5) gives

$$Ve = \frac{4d^2 c^2 \beta^2}{kR^2} m_0 (1 + \frac{1}{6}\beta^2)(1 - \beta^2)^{-1/2}. \quad (16)$$

Equating right members of (15) and (16) we obtain

$$R^2 = \frac{20d^2 \beta^2 (1 + \frac{1}{6}\beta^2)(1 - \beta^2)^{-1/2}}{3k[(1 - \beta^2)^{-1/2} (1 + \frac{1}{3}\beta^2) - 1]}. \quad (17)$$

Using Walker's expression for m_l and the above value of R^2 in equation (8) we get

$$y = \frac{10H}{3ck} \frac{e}{m_0} \frac{d^2 \beta}{[(1 - \beta^2)^{-1/2} (1 + \frac{1}{3}\beta^2) - 1]}. \quad (18)$$

These values of R and y are listed in columns 5 and 9 of Table I. The corresponding curve is indicated by "W" in fig. 2.

The Bucherer-Langevin Theory.

Assuming constant volume of the deformed electron, the expressions for the two masses of the electron as developed by Bucherer-Langevin‡ are :

$$m_t = m_0(1 - \beta^2)^{-1/3},$$

$$m_l = m_0(1 - \beta^2)^{-4/3}(1 - \frac{1}{3}\beta^2).$$

* Walker, Proc. Roy. Soc. A 93, p. 448.

† Schott, Proc. Roy. Soc. A 94, p. 442.

‡ Bucherer-Langevin, *Phys. Zeit.* vii. p. 302.

Substituting this value of m_t in equation (1) we have

$$Ve = \int_0^\beta m_0 c^2 (1 - \beta^2)^{-1/2} (1 - \frac{1}{3}\beta^2) \beta d\beta. \quad (19)$$

Integrating by parts this becomes

$$Ve = \frac{3}{4} c^2 (m_t - m_0) + \frac{1}{4} \beta^2 c^2 m_t. \quad (20)$$

Substituting the Bucherer-Langevin expression for m_t in equation (5) and combining with (20) we obtain

$$R^2 = \frac{16d^2\beta^2}{k[3 - 3(1 - \beta^2)^{1/2} + \beta^2]}. \quad (21)$$

Substitution in (8) now gives

$$y = -\frac{H \frac{e}{m_0} R^2 (1 - \beta^2)^{1/2}}{2c\beta}. \quad (22)$$

The values of R and y calculated by the use of (21) and (22) are placed in columns 4 and 8 of Table I. The corresponding curve, "B-L," is shown in fig. 2.

Abraham's Theory.

Assuming a rigid spherical electron Abraham* has derived the following:

$$m_t = \frac{3}{4} \frac{m_0}{\beta^2} \left[\frac{1 + \beta^2}{2\beta} \log_e \frac{1 + \beta}{1 - \beta} - 1 \right],$$

$$m_l = \frac{3}{4} \frac{m_0}{\beta^2} \left[-\frac{1}{\beta} \log_e \frac{1 + \beta}{1 - \beta} + \frac{2}{1 - \beta^2} \right].$$

Substituting his value of m_t in equation (1) we have

$$Ve = \frac{3}{4} m_0 c^2 \int_0^\beta \frac{1}{\beta} \left[-\frac{1}{\beta} \log_e \frac{1 + \beta}{1 - \beta} + \frac{2}{1 - \beta^2} \right] d\beta,$$

$$Ve = \frac{3}{4} m_0 c^2 \left\{ \int_0^\beta -\frac{1}{\beta^2} \log_e \frac{1 + \beta}{1 - \beta} d\beta + \int_0^\beta \frac{2}{\beta(1 - \beta^2)} d\beta \right\}. \quad (23)$$

On integrating the first term by parts the equation simplifies readily and becomes

$$Ve = \left[\frac{3m_0 c^2}{4\beta} \log_e \frac{1 + \beta}{1 - \beta} \right]_0^\beta. \quad (24)$$

* Abraham, *Ann. d. Phys.* x. p. 105.

Expanding in series and substituting limits

$$Ve = \frac{3m_0c^2}{2} \left[\frac{1}{2\beta} \log_e \frac{1+\beta}{1-\beta} - 1 \right]. \quad (25)$$

Placing Abraham's expression for m_t in equation (5) we have

$$Ve = \frac{3m_0c^2d^2}{2kR^2} \left[\frac{1+\beta^2}{\beta} \log_e \frac{1+\beta}{1-\beta} - 2 \right]. \quad (26)$$

Equating right members of (25) and (26) we get

$$R^2 = \frac{\frac{d^2}{k} \left[\frac{1+\beta^2}{\beta} \log_e \frac{1+\beta}{1-\beta} - 2 \right]}{\frac{1}{2\beta} \log_e \frac{1+\beta}{1-\beta} - 1}. \quad (27)$$

Substituting Abraham's value of m_t and the above value of R^2 in equation (8) we obtain

$$y = \frac{2H \frac{e}{m_0} R^2 \beta}{3c \left[\frac{1+\beta^2}{2\beta} \log_e \frac{1+\beta}{1-\beta} - 1 \right]}. \quad (28)$$

These values of R and y are listed in columns 3 and 7 of Table I. The curve is designated by "A" in fig. 2.

The maximum voltage applied cannot exceed 2×10^5 volts. The curves are plotted as solid lines for velocities up to $\beta = .7$, as this is the region that will be covered experimentally. The curves are continued as dotted lines up to $\beta = .9$.

The terminal points of the curves indicate that the application of a constant voltage and zero magnetic field could also be used as a test. The resulting trace on the photographic film would then be a single spot, the distance of the spot from the source enabling the experimenter to determine which of the theories is most nearly correct. It is readily seen, however, that this test becomes the more delicate only in the region $\beta = .9$. This region cannot be explored at the present time.

Department of Physics,
University of California.

LXXV. *Does an accelerated Electron necessarily radiate Energy on the Classical Theory?* By G. A. SCHOTT, B.A., D.Sc., F.R.S., Professor of Applied Mathematics, University College of Wales, Aberystwyth*.

1. **I**N a paper † and a letter ‡, published under the above title, S. R. Milner has referred to a solution of mine of the problem of the motion of a Lorentz electron in a uniform electric field, when the motion is parallel to the lines of force of the field. It is a special case of the more general problem of the monoclinoidal motion of an electron solved in my Adams Prize Essay of 1908, but treated more completely in my book on Electromagnetic Radiation in §§151–154, as regards the motion itself, and §§43–60, as regards the electromagnet field produced by it. In my book (quoted below as E.R.) no account was taken of the effect of the reaction due to radiation, beyond an estimate of the numerical error in E.R. § 154; but in a later paper in this journal § I worked out the effect of the radiation pressure completely for the special case considered by Milner. The result was unexpected: the radiation pressure was found to be zero, provided that Newton's First and Second Laws of Motion were assumed to be true when the velocity of the electron was infinitely small compared with that of light. The explanation is simple; there is an irreversible radiation of energy at the rate R given by the well-known formula of Liénard and Abraham, but this is not all. There is also a reversible radiation at the rate $-\dot{Q}$, where $Q = 2ce^2(\ddot{\mathbf{v}}\mathbf{v})/3(c^2 - v^2)^2$; $-\dot{Q}$, being a function of the motion of the electron alone and representing energy stored in it, may be called its acceleration energy. Calculation shows that $R - \dot{Q}$ is identically zero, so that the whole of the energy radiated irreversibly between any two times is derived from the acceleration energy, whilst all the work done by the electric field goes to increase the kinetic energy of the electron. Thus on the whole no energy is radiated in any interval whatsoever.

2. This result is in complete agreement with one of the

* Communicated by the Author.

† S. R. Milner, *Phil. Mag.* vol. xli. p. 405 (1921) (quoted below as M1).

‡ S. R. Milner, *Phil. Mag.* vol. xlv. p. 1052 (1922) (quoted below as M2).

§ G. A. Schott, *Phil. Mag.* vol. xxix. p. 49 (1915) (quoted below as S).
Phil. Mag. S. 6. Vol. 45. No. 268. April 1923 3 D

conclusions drawn by Born * in his 1909 paper on the Theory of the rigid Electron in the Kinematics of the Principle of Relativity, referred to by Milner in his letter (M2); but the point of view of Born is so different from mine that at the time I did not realize the connexion between his investigation and mine, otherwise I should have referred to his paper in my book as well as my last paper (S). Nevertheless there are some points of difference, to which it is worth while to draw attention, due in the main to the fact that Born takes the standpoint of an observer moving with the electron, whilst mine is that of a fixed observer, who studies the motion of the electron relative to himself. Consequently Born finds that the components of the 4-vector potential of the Special Relativity Theory for the fixed observer can be expressed in terms of those of a "resting" 4-vector potential, relative to the moving observer, by means of a linear transformation of the Lorentz type, when the motion is that of our special case, identical with Born's "hyperbolic" motion. Moreover the "resting" 4-vector potential depends only on the three parameters of the world line of the fieldpoint under consideration and not at all on the fourth parameter, which determines the position of the field point on its world line; Born concludes that the electron carries its electromagnetic field with it. He also deduces the result that the magnetic force, and therefore also the Poynting vector, vanishes for the moving observer, so that to him the electron does not appear to radiate. This result is hardly surprising in view of the fact that the electron always remains at rest and invariable in form for this observer. But I can find no proof in Born's paper, nor have I been able to find one anywhere else, that the vanishing of the Poynting vector relative to an observer moving with an electron which executes a "hyperbolic" motion necessarily entails the cancelling of the irreversible by the reversible radiation for a fixed observer; thus the formal proof that this does take place, given in (S), seems to be necessary.

3. Again in §13 of his paper Born proves that the term of zero order in the dimensions of the electron occurring in the expression for the mechanical force, *i. e.*, what I have called the radiation pressure, vanishes identically. This term involves Born's coefficient μ_1 as a factor, but in evaluating it the assumption is made that the electron appears to an observer moving with it to possess spherical symmetry. This limitation is unnecessary, for the radiation pressure is

* Born, *Annalen der Physik*, iii. p. 1 (1909).

independent of the structure of the electron, a fact already known to Abraham.

4. Returning now to Milner's first paper (M 1) we note that his interesting modification of the problem considered so far is one in which two electrons, equal in every respect but with charges of opposite sign, are moving in the same straight line with equal but opposite velocities and accelerations. In this modification there is no radiation because of the quasisymmetry of the electromagnetic field, due to the annihilation of the boundary $x+ct=0$, but this proves nothing as to the radiation from a single accelerated electron. The absence of radiation in Milner's case seems to me somewhat analogous to the reduction of the radiation from a revolving ring of equidistant electrons owing to the superposition of the electromagnetic fields of the different electrons of the ring; but whereas in Milner's case the superposition of the fields annihilates the radiation completely, it does so only partially in the case of the ring.

5. In the same paper (M 1, p. 417) Milner raises a fundamental question as to the meaning of the undoubted fact that there is on the whole a flow of energy from the moving boundary $x+ct=0$ into the electromagnetic field of the accelerated electron, and concludes that "the solution premises an initial intrinsic energy in the boundary, apart from that of the electronic field." This conclusion does not appear to me to be warranted, for there must be an electromagnetic field beyond the moving boundary, due to the past history of the accelerated electron; I shall now prove that whatever that past history may have been, provided only that the velocity of the electron has been a continuous function of the time, the electromagnetic field beyond the moving boundary supplies the boundary with precisely the amount of energy needed to compensate the flow of energy into the electronic field. Let us begin by calculating the flow in question.

The line of electric force due to the electron, $\chi=\text{constant}$, is a circle of radius $\xi \operatorname{cosec} \chi$, of which the centre is the point $(0, \xi \cot \chi)$, and the line of the Poynting flux is the orthogonal circle. Hence the sine of the angle made by the line of force with the axis of x is numerically equal to $x \sin \chi / \xi$, which reduces to $ct \sin \chi / \xi = \beta \sin \chi$ at the moving boundary. It follows from Milner's equation (4), (M 1, p. 406) that at the moving boundary $E_y = \beta \sin \chi \cdot E = H$. The rate at which the moving boundary lays down energy behind it is $c(E^2 + H^2)/8\pi$, when there is no external field, or $c(\{E_x + X\}^2 + E_y^2 + H^2)/8\pi$ when there is. The latter

expression reduces to $c\{E_x + X\}^2 + 2H^2/8\pi$ in virtue of the relation just proved. The component of the Poynting flux normal to the boundary is equal to $cE_y H/4\pi = cH^2/4\pi$ by the same relation, and it is from the electronic field towards the boundary. Hence the total rate at which the electronic field gains energy from the boundary is the difference between these two quantities and is equal to $c\{E_x + X\}^2/8\pi$.

But $E_x + X$ is the flux of electric induction from the boundary into the electronic field reckoned per unit area. The boundary represents an infinitely thin transition layer; the electric and magnetic forces in it are everywhere finite, and it is uncharged. Therefore there can be no flux of induction along it, and there must be a flux of induction into it from the region outside the electronic field exactly compensating the first flux, $E_x + X$. Thus there must be a field outside, such that the normal electric force is the same on both sides of the moving boundary. This outside field is that due to the motion of the electron which existed before the establishment of the external electric field X producing the accelerated motion, and like all fields due to the motion of a single electron it possesses the property that the component of the electric force tangential to its boundary is exactly equal to the magnetic force, a result which follows from the usual point-law (*cf.* M 1, p. 416, or E. R., p. 23, equations 32 and 33). Hence there is on the whole a loss of energy from the outside field to the moving boundary equal to $c\{E_x + X\}^2/8\pi$, per second, precisely equal to the gain of the inside electronic field. It should be noted that if the velocity of the electron be suddenly changed as well as its acceleration, this is no longer true; for then an X -ray pulse is generated, inside which the electric and magnetic forces are very intense, so that there is a finite flux of induction along it, and the normal electric forces on the two sides of the pulse are no longer equal.

6. In conclusion, the whole question of the radiation from a single accelerated electron will be put in a clearer light by solving the following problem:—Required to find the conditions under which an accelerated electron will not radiate energy on the whole and will move as if there were no radiation, in the usual sense of irreversible radiation. This problem is most easily attacked by the method used in the paper already referred to (S, §§ 3, 4).

For the sake of simplicity we shall use as units of mass, length, and time respectively the following quantities: the resting mass of the electron, $m = 8.76 \cdot 10^{-28}$ gram, the

conventional radius of the resting surface electron, $2e^2/3c^2m = 1.83.10^{-13}$ cm., and, lastly, $2e^2/3c^3m = 6.1.10^{-24}$ sec. Instead of the time t we shall use the time variable τ , defined by the equation $\tau = \int_0^t \sqrt{1-v^2} dt$, where v is the velocity of the electron referred to that of light as the appropriate new unit. We shall use an accent to denote differentiation with respect to τ , and further shall write $\mathbf{w} = \mathbf{r}' =$ vector velocity referred to time τ . Then the equation of motion of the electron under force $\mathbf{F}$ may be written in the form (S, p. 52, equations (43) and (44))

$$\mathbf{w}' - \mathbf{w}'' + R\mathbf{w} = \mathbf{F} \sqrt{1+w^2} \quad . \quad . \quad . \quad (1)$$

where R is the irreversible radiation and is given by

$$R = \mathbf{w}'^2 - \frac{(\mathbf{w}\mathbf{w}')^2}{1+w^2} \quad . \quad . \quad . \quad (2)$$

The first term on the left of (1) represents the usual effective force on the electron, whilst the last two represent the radiation pressure; when the radiation has no effect on the motion, the last terms cancel each other, and the equation breaks up into two:—

$$\mathbf{w}'' = \left\{ \mathbf{w}'^2 - \frac{(\mathbf{w}\mathbf{w}')^2}{1+w^2} \right\} \mathbf{w} \quad . \quad . \quad . \quad (3)$$

and

$$\mathbf{w}' = \mathbf{F} \sqrt{1+w^2} \quad . \quad . \quad . \quad (4)$$

Multiplying (3) vectorially by $\mathbf{w}$ we obtain in succession

$$[\mathbf{w}\mathbf{w}''] = 0, [\mathbf{w}\mathbf{w}'] = \mathbf{C}, (\mathbf{C}\mathbf{w}) = 0, (\mathbf{C}\mathbf{r}) = D,$$

where $\mathbf{C}$ is a vector constant, and D a scalar constant. The last equation is that of a plane, so that the orbit of the electron must be a plane curve.

7. Let us take the plane of the orbit as the x, y plane, and let ψ denote the angle between the forward direction of motion and the axis of x ; then we have $x' = w \cos \psi$, $y' = w \sin \psi$, so that x', y', w, ψ take the place of x, y, r, θ in plane polar coordinates. The second equation of the last set takes the place of the equation of angular momentum and may be written in the form

$$x'y'' - x''y' = w^2\psi' = C \quad . \quad . \quad . \quad (5)$$

The radial component of $\mathbf{w}''$ is $w'' - \psi'^2 w$, the value of $\mathbf{w}'^2$ is $w'^2 + w^2\psi'^2$, and that of $(\mathbf{w}\mathbf{w}')$ is wu' . Hence the tangential component of the vector equation (3) reduces to

$$w'' - w\psi'^2 = \left\{ w'^2 + w^2\psi'^2 - \frac{w^2w'^2}{1+w^2} \right\} w.$$

Using (5) we may write this in the form

$$w'' - \frac{ww'^2}{1+w^2} - C^2 \frac{1+w^2}{w^3} = 0.$$

An integrating factor of this equation is given by $2w'/(1+w^2)$; performing the integration we obtain

$$\frac{w'^2}{1+w^2} + \frac{C^2}{w^2} = A. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

At this stage it will be convenient to introduce new arbitrary constants in place of A and C; we shall write

$$A = a^{-2}, \quad C = -ba^{-2}. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Then equations (5) and (6) may be written in the forms

$$w^2 \psi' = -ba^{-2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

$$a^4 w^2 w'^2 = (1+w^2)(a^2 w^2 - b^2). \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Writing $\tau = a\phi$ for shortness' sake we obtain from (9)

$$a^2 w^2 = b^2 \cosh^2 \phi + a^2 \sinh^2 \phi. \quad . \quad . \quad . \quad (10)$$

Substituting in (8) and integrating we obtain

$$\psi = - \int^{\phi} \frac{ab d\phi}{b^2 \cosh^2 \phi + a^2 \sinh^2 \phi} = \tan^{-1}(b \coth \phi/a). \quad . \quad (11)$$

where the constants of integration have been chosen so as to make w, ψ equal to $b/a, \pi/2$ respectively when ϕ and τ vanish, a choice which merely amounts to a suitable determination of the time origin and the axes, and of course involves no loss of generality.

The time t is given in terms of ϕ by the equation

$$t = \int_0^{\tau} \sqrt{1+w^2} d\tau = \sqrt{(a^2+b^2)} \int_0^{\phi} \cosh \phi d\phi = \sqrt{(a^2+b^2)} \sinh \phi. \quad . \quad . \quad . \quad (12)$$

At this stage it will be convenient to change back to t as independent variable; we have

$$\begin{aligned} \dot{x} &= x'/\sqrt{1+w^2} = w \cos \psi / \sqrt{1+w^2}, \\ \dot{y} &= w \sin \psi / (1+w^2). \end{aligned}$$

From (10) and (11) we find

$$\begin{aligned} w \cos \psi &= \sinh \phi, \quad w \sin \psi = b \cosh \phi/a, \\ \sqrt{1+w^2} &= \sqrt{(a^2+b^2)} \cosh \phi/a. \end{aligned}$$

From (12) we obtain

$$\dot{x} = \frac{at}{\sqrt{(a^2+b^2)}\sqrt{(a^2+b^2+t^2)}}, \quad \dot{y} = \frac{b}{\sqrt{(a^2+b^2)}}. \quad . \quad (13)$$

Integrating equations (13) and choosing the constants of integration suitably we obtain

$$x = \frac{a\sqrt{(a^2 + b^2 + t^2)}}{\sqrt{(a^2 + b^2)}}, \quad y = \frac{bt}{\sqrt{(a^2 + b^2)}} \dots (14)$$

Eliminating t we find that the orbit is the hyperbola

$$\frac{x^2}{a^2} - \frac{y^2}{b^2} = 1,$$

described with a constant component velocity parallel to the transverse axis equal to $b/\sqrt{(a^2 + b^2)}$.

8. The resultant velocity, v , is given from (13) by

$$v = \frac{\sqrt{(b^2 + t^2)}}{\sqrt{(a^2 + b^2 + t^2)}} \dots (15)$$

Thus we obtain

$$\sqrt{(1 - v^2)} = \frac{a}{\sqrt{(a^2 + b^2 + t^2)}} \dots (16)$$

The components of the momentum in the present units are found from (13) and (16) to be

$$\frac{\dot{x}}{\sqrt{(1 - v^2)}} = \frac{t}{\sqrt{(a^2 + b^2)}}, \quad \frac{\dot{y}}{\sqrt{(1 - v^2)}} = \frac{b\sqrt{(a^2 + b^2 + t^2)}}{a\sqrt{(a^2 + b^2)}}.$$

Hence the components of the mechanical force on the electron are

$$X = \frac{1}{\sqrt{(a^2 + b^2)}}, \quad Y = \frac{bt}{a\sqrt{(a^2 + b^2)}\sqrt{(a^2 + b^2 + t^2)}} = \frac{y}{x} X \dots (17)$$

Thus the mechanical force needed to generate the motion is central with a constant component parallel to the real axis of the hyperbolic orbit. It is clearly not derivable from a potential, so that it cannot be produced by an electrostatic field alone, but it can be produced by a uniform electrostatic field of intensity E parallel to the axis of x , combined with a uniform magnetic field of intensity H parallel to the negative direction of the axis of z , *i. e.* perpendicular to the plane of the orbit. In order to see this let us for simplicity sake take the charge of the electron as unit charge; then we have by (13) and (14)

$$X = E - \dot{y}H = E - \frac{bH}{\sqrt{(a^2 + b^2)}},$$

$$Y = \dot{x}H = \frac{atH}{\sqrt{(a^2 + b^2)}\sqrt{(a^2 + b^2 + t^2)}}$$

or
$$Y = \frac{a^2Hy}{bx} X.$$

Comparing these equations with (17) we obtain

$$H = ba^{-2}, \quad E = a^{-2} \sqrt{(a^2 + b^2)}. \quad (18)$$

We must bear in mind that the units are not the usual ones; a, b are lengths measured in terms of the unit $2e^2/3c^2m$; X, Y are mechanical forces measured in terms of the unit $3c^4m^2/2e^2$; finally, E, H are measured in terms of units which are $3c^4m^2/2e^3$ times the electrostatic and magnetic units respectively. This factor is numerically equal to 9.10^{15} . If a', b', H', E' be the values of the semiaxes of the orbit and of the magnetic and electric forces measured in centimetres and in magnetic and electrostatic units respectively, then a', b' are $2e^2/3c^2m$ times a, b and H', E' are $3c^4m^2/2e^3$ times H, E respectively, so that $H' = c^2mb'/ea'^2$, with a similar expression for E' . When b is zero, the mechanical force reduces to $eE' = c^2m/a'$, the value for the special case considered by Milner (M1, p. 406 (2)), where m_0 is used instead of our m , and k instead of our a' .

9. It remains for us to consider the energy relations of the motion. The kinetic energy T is given by the usual relation together with (16); we obtain

$$T = \frac{1}{\sqrt{(1-v^2)}} - 1 = \frac{\sqrt{(a^2 + b^2 + t^2)}}{a} - 1, \quad \dot{T} = \frac{t}{a\sqrt{(a^2 + b^2 + t^2)}}. \quad (19)$$

The rate of working of the applied force is found from (13) and (17) to be given by

$$X\dot{x} + Y\dot{y} = \frac{t}{a\sqrt{(a^2 + b^2 + t^2)}} = \dot{T}.$$

Thus the whole work done on the electron by the external field is transformed into kinetic energy, just as if there were no radiation. Again the rate at which the electron radiates energy irreversibly is given by the usual expression of Liénard (S, p. 51 (7)), which in our units reduces to

$$R = \frac{\dot{\mathbf{v}}^2}{(1-v^2)^2} + \frac{(\mathbf{v}\dot{\mathbf{v}})^2}{(1-v^2)^3}. \quad (20)$$

We see from (13) that $\ddot{x} = a\sqrt{(a^2 + b^2)}/(a^2 + b^2 + t^2)^{3/2}$, $\ddot{y} = 0$, so that $\dot{\mathbf{v}}^2 = \ddot{x}^2$, and $(\mathbf{v}\dot{\mathbf{v}}) = \dot{x}\dot{x}$; hence we obtain from (20), with (16),

$$R = \frac{(1-\beta^2)\ddot{x}^2}{(1-v^2)^3} = \frac{1}{a^2}. \quad (21)$$

Thus the electron radiates energy irreversibly at a constant rate.

Lastly, the acceleration energy, $-Q$, is given in our units by the following equation (*cf.* S, p. 51 (6))

$$Q = \frac{(\mathbf{v}\mathbf{v})}{(1-v^2)^2} = \frac{\dot{x}\dot{x}}{(1-v^2)^2} = \frac{t}{a^2} \dots \dots (22)$$

Comparing this equation with (21) we see that $R-Q=0$.

Thus the irreversible loss of energy by radiation is exactly defrayed from the loss of acceleration energy of the electron, just as it was found to be in the special case of the hyperbolic motion (S, § 8) already referred to.

The accelerated motions just considered are particularly interesting on account of this property of emitting no radiation on the whole, and we have proved that they are unique in this respect. It must be noted particularly that they do not help us in any way to remove the existing contradiction between the invariable irreversible loss of energy, due to radiation from an electron describing a closed orbit, required by classical electrodynamics, and the total absence of radiation in stationary motions of electrons postulated by Bohr. It is otherwise evident that the acceleration energy of an electron describing a stationary orbit, depending as it does on the state of the electron alone, must repeat its values as that state repeats itself, and cannot therefore provide a reservoir from which the irreversible part of the radiation can be defrayed permanently. On this question reference may be made to a former communication* and to a paper by H. Bateman †, in which the writer's conclusions are confirmed.

10. The chief conclusions of the present paper may be summarized as follows:—

(1) The hyperbolic motion of the electron considered in (S) and (M1) involves no contradiction with the Principle of the Conservation of Energy provided that it be generated in any way which is consistent with the conservation of its electric charge and the continuity of its velocity.

(2) The only class of motions unaffected by radiation is that in which the path of the electron is an hyperbola described with a constant component velocity parallel to the conjugate axis. The hyperbolic motion of Born is a special case in which the transverse velocity is zero. In these motions the radiation is defrayed entirely at the expense of the acceleration energy of the electron.

* Schott, *Phil. Mag.* vol. xxxvi. p. 243 (1918).

† Bateman, *Nat. Acad. Sci., Proc.* 5, p. 367 (1919).

LXXVI. *The Disturbance of the Uniform Temperature of the Stratosphere by the Vertical Displacement associated with Horizontal Motion governed by the "Geostrophic Law."*
By F. J. W. WHIPPLE, M.A., F.Inst.P.*

§ 1. **I**N his work on 'Weather Prediction by Numerical Process' †, Mr. L. F. Richardson has devoted much attention to the results which follow from the assumption that the flow of air is governed by the law that the "geostrophic force" due to the earth's rotation balances exactly the pressure gradient.

The analysis appropriate for the general motion of the atmosphere is necessarily complicated, and therefore special interest is attached to a very neat formula given ‡ by Mr. Richardson, by which certain processes taking place in the stratosphere are related.

The formula in question is such that it can be tested by the comparison of the records of wind velocity and of air temperature. A preliminary test was made in Mr. Richardson's book, and many more are given in a recently published paper § entitled "An observational test of the geostrophic approximation in the Stratosphere," in which he collaborated with Drs. Wagner and Dietzius.

The following investigation, which was undertaken with the intention of supplying a simple proof of Richardson's formula, has led to the discovery that the formula is incomplete and that the term which had been overlooked is of considerable importance.

§ 2. The problem to be investigated may be set out as follows:—It being assumed (1) that the horizontal movement of the air is at all times given precisely by the "geostrophic law" ‖, (2) that the distribution of temperature

* Communicated by the Author.

† Cambridge University Press, 1922.

‡ *L. c.* page 144, equation 18.

§ London R. Met. Soc. Q. J. 1922, p. 328.

‖ Sir Napier Shaw writes as follows ('Manual of Meteorology,' part iv. p. 4: Cambridge University Press, 1919):—"The function of pressure-distribution seems rather to be to steer the air than to speed it or stop it. So it will be more profitable to consider the 'strophic' balance between the flow of air and the distribution of pressure as an axiom or principle of atmospheric motion. . . . This principle was enunciated in a paper before the Royal Society of Edinburgh in 1913 as follows:—*In the upper layers of the atmosphere the steady horizontal motion of the air at any level is along the horizontal section of the isobaric surface at that level and the velocity is inversely proportional to the separation of the isobaric lines in the level of the section.*"

in the stratosphere at a particular instant is independent of height though not uniform in a horizontal plane, and (3) that the effects of radiation and eddy conductivity may be ignored; what will be the initial rate of change of temperature?

To solve the problem we have to express in mathematical form the laws of conservation of mass and conservation of energy.

The conservation of mass implies that the rate of increase of density in an elementary volume moving with the air is accounted for by the excess of inflow over outflow. As regards vertical movement, the excess is $-\rho \frac{\partial V_H}{\partial h}$ (ρ being the density, V_H the upward velocity, and h being measured upwards). As regards horizontal movement we notice that when the dependence of the geostrophic factor $2\omega \sin \phi$ on latitude is ignored, the assumption that the horizontal velocity is "geostrophic" implies stream-line motion with no accumulation of matter anywhere. To make allowance for the latitude variation we need consider only the northward component of velocity, for which the equation

$$V_N = \frac{1}{2\omega \sin \phi} \cdot \frac{1}{\rho} \cdot \frac{\partial p}{\partial e} \dots \dots \dots (1)$$

holds. (ω is the angular velocity of the earth, ϕ the latitude, and $\frac{\partial p}{\partial e}$ is the east-gradient of pressure.)

The increase of V_N towards the north on account of the variation of ϕ is given by the equation

$$\frac{1}{V_N} \cdot \frac{\partial' V_N}{\partial n} = -\frac{1}{\sin \phi} \cdot \frac{\partial \sin \phi}{\partial n} = -\frac{\cot \phi}{a} \dots \dots (2)$$

(a is the radius of the earth, $dn = a d\phi$, and the notation $\frac{\partial' V_N}{\partial n}$ is used to indicate that only the variation of V_N dependent on the variation of $\sin \phi$ is considered).

Accordingly the equation representing the conservation of mass is

$$\frac{D\rho}{Dt} = -\rho \left[\frac{\partial V_H}{\partial h} - V_N \frac{\cot \phi}{a} \right] \dots \dots (3)$$

By hypothesis the effects of radiation etc. are excluded, so that the conservation of energy is represented by the

780 Mr. F. J. W. Whipple on the *Disturbance of the*
adiabatic conditions :

$$\frac{1}{\gamma_v} \frac{D}{Dt} (\log p) = \frac{1}{b} \frac{D}{Dt} (\log \theta) = \frac{1}{\gamma_p} \frac{D}{Dt} (\log p), \quad (4)$$

in which γ_v , γ_p are the capacities for heat of air at constant volume and constant pressure (in dynamical measure) and b is the "gas constant," so that $\gamma_p - \gamma_v = b$.

Now

$$\frac{D}{Dt} (\log \theta) = \left(\frac{\partial}{\partial t} + V_H \frac{\partial}{\partial h} \right) \log \theta + \left(V_E \frac{\partial}{\partial e} + V_N \frac{\partial}{\partial n} \right) \log \theta, \quad (5)$$

and since the horizontal wind is geostrophic

$$V_N = \frac{1}{2\omega \sin \phi} \cdot \frac{1}{\rho} \cdot \frac{\partial p}{\partial e} = \frac{\theta \cdot b}{2\omega \sin \phi} \frac{\partial}{\partial e} (\log p), \quad (6)$$

whilst

$$V_E = - \frac{1}{2\omega \sin \phi} \cdot \frac{1}{\rho} \frac{\partial p}{\partial n} = - \frac{\theta \cdot b}{2\omega \sin \phi} \frac{\partial}{\partial n} (\log p). \quad (7)$$

It follows that

$$\frac{1}{b} \frac{D}{Dt} (\log \theta) = \frac{1}{b} \left(\frac{\partial}{\partial t} + V_H \frac{\partial}{\partial h} \right) \log \theta + \frac{1}{2\omega \sin \phi} \frac{\partial (\log p, \theta)}{\partial (e, n)}. \quad (8)$$

In writing down the corresponding equation for variation of p , we notice (1) that the horizontal motion, being along the isobars, does not necessitate any change of pressure, and (2) that to a close approximation, vertical accelerations being small in comparison with g ,

$$\frac{\partial}{\partial h} (\log p) = - \frac{g}{b\theta}. \quad (9)$$

Accordingly we have

$$\frac{D}{Dt} (\log p) = \frac{\partial}{\partial t} (\log p) - V_H \frac{g}{b\theta}. \quad (10)$$

§ 3. The foregoing equations do not involve the assumption as to the uniformity of temperature in the stratosphere.

We now follow Richardson and suppose that $\frac{\partial \theta}{\partial h} = 0$ holds instantaneously, but that $\frac{\partial \theta}{\partial t}$ and its derivatives do not vanish.

Under these conditions differentiation of the formulæ leads to simplification.

The relations we propose to utilise are derived from (4), viz. :—

$$\frac{1}{\gamma_v} \frac{\partial}{\partial h} \frac{D}{Dt} (\log \rho) = \frac{1}{b} \frac{\partial}{\partial h} \frac{D}{Dt} (\log \theta) \quad . \quad . \quad (11)$$

and

$$\frac{1}{\gamma_p} \frac{\partial^2}{\partial h^2} \frac{D}{Dt} (\log p) = \frac{1}{b} \frac{\partial^2}{\partial h^2} \frac{D}{Dt} (\log \theta). \quad . \quad . \quad (12)$$

On substitution of the appropriate terms from (3), (8), and (10) these relations become

$$-\frac{1}{\gamma_v} \left[\frac{\partial^2 V_H}{\partial h^2} - \frac{\partial V_N}{\partial h} \frac{\cot \phi}{a} \right] = \frac{1}{b} \frac{\partial}{\partial h} \frac{\partial}{\partial t} (\log \theta) \quad (13)$$

and

$$\frac{1}{\gamma_p} \frac{g}{b\theta} \left[\frac{\partial}{\partial h} \frac{\partial}{\partial t} \log \theta - \frac{\partial^2 V_H}{\partial h^2} \right] = \frac{1}{b} \frac{\partial^2}{\partial h^2} \frac{\partial}{\partial t} \log \theta. \quad (14)$$

Proceeding to eliminate $\frac{\partial^2 V_H}{\partial h^2}$ we obtain the relation

$$\frac{b}{\gamma_p} \frac{\cot \phi}{a} \frac{\partial V_N}{\partial h} = \frac{\partial}{\partial h} \frac{\partial}{\partial t} \log \theta - H \frac{\partial^2}{\partial h^2} \frac{\partial}{\partial t} \log \theta, \quad . \quad (15)$$

where H is written for $\frac{b\theta}{g}$ or $\frac{p}{g\rho}$ the height of the “homogeneous atmosphere” at the temperature θ .

The term in H is the one which was overlooked * by Mr. Richardson.

§ 4. The interest in this formula (15) appears to be mainly theoretical in that it shows one way in which temperature differences would arise in the stratosphere, even if there were complete uniformity to begin with. An observational test is hardly a fair one unless due allowance is made for any departures from uniformity that may be known.

* The error can be traced to the omission of a term $\gamma_p \frac{\partial}{\partial t} \left(\frac{\partial \log \theta}{\partial h} \right)$ from the left of equation (10) on p. 142 of ‘Weather Prediction by Numerical Process.’ In passing from (9) to (10) it is not legitimate to use (7) and differentiate with respect to the time, for (7) is proved on the assumption that $\frac{\partial \theta}{\partial h} = 0$, and is therefore only valid as a statement of the initial conditions. The disappearance of the term $\tan \phi$ from Mr. Richardson’s equation (10) is in accordance with the Met. Soc. paper (l. c. p. 329).

In arriving at (15) it was not only assumed that $\frac{\partial \theta}{\partial h}$ was zero, but also that its differential coefficients with respect to h and e and n were zero. If these assumptions are not made then (15) must be replaced by a much more complicated relation: and the terms between which comparison has to be made are not only $\frac{\partial}{\partial h} \frac{\partial}{\partial t} \log \theta$ and $H \frac{\partial^2}{\partial h^2} \frac{\partial}{\partial t} \log \theta$, but also such as

$$V_H \frac{\partial^2}{\partial h^2} \log \theta, H V_H \frac{\partial^3 \log \theta}{\partial h^3}, V_N \frac{\partial^2 \log \theta}{\partial n \partial h}, \text{ and } V_N H \frac{\partial^3 \log \theta}{\partial n \partial h^2}.$$

In the examples collected by Richardson, Wagner, and Dietzius, $\frac{\partial}{\partial h} (\log \theta)$ is not usually zero, and there is no reason to suppose that these terms, which represent the irregular space distribution of $\frac{\partial}{\partial h} (\log \theta)$, are small in comparison with the terms which represent the rate at which it is changing.

In the circumstances the coefficient computed by these authors for the correlation between the term on the left of equation (15) and the first term on the right is higher than one would expect.

§ 5. In conclusion, it may be remarked that the general equations (4), in which V_H and $\frac{\partial V_H}{\partial h}$ occur implicitly, as may be seen by comparison with equations (3), (8), and (10), provide opportunities for comparison of theory and observation. Observations of V_H up to very great heights by the pilot-balloon method are not numerous, but they should serve for the purpose. It will be noticed that the equations mentioned hold good for the troposphere, and therefore that the investigation can refer to the region in which the observations of temperature are being made day by day instead of to the higher layers which are only reached occasionally by balloons.

LXXVII. *Note on the Calculation of High-Frequency Inductances.* By F. B. PIDDUCK *.

THE present note has been suggested by certain experiments†, in which the self-inductance of a circular ring of rectangular cross-section was measured for oscillatory currents of medium frequency. A rough estimate of the theoretical inductance can be found by taking the inductance for low frequency from Maxwell's or Weinstein's formula and correcting as for a circular cross-section of equal area. The principles on which a solution of the general problem is to be sought have been stated by Rayleigh‡ and Curtis§. Rayleigh's method (easily generalized to any frequency and cross-section) is the more powerful, but will not give the self-inductance without prohibitive labour, unless the frequency is low. There is, however, one case of extreme simplicity, that of a thin ring (of any cross-section) at very high frequency. I propose to show how the self-inductance can be found when the distribution of static electricity on a long bar of the same cross-section is known.

The theory is based most simply on an argument of Maxwell||, quoted by Rayleigh. Suppose that the inducing field is confined to a region which may interlace the ring, but does not cut into it, so that the impressed magnetic force vanishes at all points of the metal. The induced currents then have no magnetic force inside the metal, and a purely tangential force at its surface. The argument applies so far to any conducting mass whatever, at sufficiently high frequency. It follows that the current in a *thin* ring is spread over the surface in such a way that the surface-density of current is proportional to the surface-density of static electricity on a long bar of the same section, the lines of magnetic force near the wire corresponding to the equipotentials. The currents are all in the same phase, a quarter period behind the inducing field. This conclusion follows also from Rayleigh's theory of waves on wires¶.

Consider for the moment a slightly more general distribution. Let u be the amplitude of current-density at a

* Communicated by the Author.

† Phil. Mag. [6] vol. xlii. p. 220 (1921).

‡ Rayleigh, Proc. Roy. Soc. A, vol. lxxxvi. p. 567 (1912); Scientific Papers, vol. vi. p. 106.

§ H. L. Curtis, Sci. Papers Bur. Standards, vol. xvi. p. 93 (1920).

|| 'Electricity and Magnetism,' 3rd ed. vol. ii. p. 290.

¶ Rayleigh, Phil. Mag. [5] vol. xlv. p. 199 (1897); Scientific Papers, vol. iv. p. 327.

point P of the cross-section. Take another point P' distant r from P in the same section, and let dS' be an element of area at P'. Write W for the logarithmic potential of the distribution u at P; that is,

$$W = \int u' \log r dS', \quad (1)$$

where u' is the value of u at P' and integration is over the whole section. The lines of current-flow at P and P' form two closed filaments whose mutual inductance M becomes logarithmically infinite as P' tends to P, and may be written $B \log r + C$, where B and C are constant for a given form of loop. The self-inductance L of the ring is twice the magnetic potential energy of the different filaments, with sign changed, for a total current unity. Thus

$$L = \iint M u u' dS dS', \quad \text{where} \quad \int u dS = 1.$$

Hence

$$L = \iint (B \log r + C) u u' dS dS' = B \int u W dS + C = B \log R + C,$$

where

$$\log R = \int u W dS. \quad (2)$$

This is a generalization of Maxwell's method of geometrical mean distance*, admitting of easy further generalization to the case of variable phase. The self-inductance is equal to the mutual inductance of two fictitious lines, the line of centroids of the cross-section and a curve running parallel to it at a distance R given by (2). Since W is constant,

$$\log R = W, \quad \text{with} \quad \int u dS = 1. \quad (3)$$

Thus $\log R$ is the true logarithmic potential of the distribution of current. It is more convenient to deal with differences of potential. Let V be the potential at a point Q outside the conductor, the conductor itself being at *zero potential*. The true logarithmic potential at Q is $W + V$, and this tends to $\log s$ as Q moves to infinity, since the total current is unity, s being the distance of Q from any finite point in the plane of the section. Hence W is the limit of $\log s - V$ as Q goes to infinity, and we are now free to use the ordinary modes of solution of the electrostatic problem in two dimensions. Using the method of conjugate functions, suppose that the space outside the cross-section (in the z -plane) is represented conformally on the outside of a circle of unit radius (in the ζ -plane), so that the two perimeters correspond, the origin in the ζ -plane being at the centre of

* 'Electricity and Magnetism,' 3rd ed. vol. ii. p. 324.

the circle. The relation between z and ζ is assumed to be known; this is what we mean by saying that the electrostatic problem has been solved. The further substitution

$$V + iU = \log \zeta$$

makes $V=0$ when $|\zeta|=1$, and gives the potential at any external point when the perimeter is at zero potential. Taking the point from which s is measured as the origin in the z -plane, $s=|z|$ and $V=\log|\zeta|$, so that

$$\log s - V = \log |z/\zeta|.$$

Hence R is the limit of $|z/\zeta|$ as Q tends to infinity. The infinitely distant parts of the two planes are similar to each other, and $|z/\zeta|$ is the ratio of the linear dimensions. The elementary lengths $|dz|$ and $|d\zeta|$ are in the same ratio. Hence we can write indifferently

$$R = \lim \left| \frac{z}{\zeta} \right| = \lim \left| \frac{dz}{d\zeta} \right|, \quad (4)$$

as may be most convenient. Thus, if the representation of the outside of the cross-section on the outside of a circle of unit radius changes distant linear dimensions in the ratio R to 1, R is the high-frequency geometrical mean distance of the section. Otherwise, R is the radius of that circular cylinder which forms, with a parallel cylindrical sheath of very large radius, a condenser of the same capacity per unit length as the wire itself, when straightened out.

The external representation of a rectangle on a circle of unit radius belongs to a class of problems treated by Schwarz*. The transformation is

$$\frac{dz}{d\zeta} = -iC \frac{(\zeta^4 - 2\zeta^2 \cos 2\alpha + 1)^{\frac{1}{2}}}{\zeta^2}, \quad . . . (5)$$

where the radical is positive at the point $\zeta=1$, and C, α are real constants. The corners of the rectangle correspond to vectorial angles $\alpha, \pi - \alpha, \pi + \alpha$ and $2\pi - \alpha$ on the unit circle. If the origin of z corresponds to $\zeta=1$, the corners are at the points $\frac{1}{2}b, \frac{1}{2}b + ic, -\frac{1}{2}b + ic$ and $-\frac{1}{2}b$ in the z -plane, where b and c are the lengths of the sides. The integral form of (5) then yields two equations for C and α in terms of b and c , which become on reduction

$$4C(E - \cos^2 \alpha K) = b, \quad 4C(E' - \sin^2 \alpha K') = c,$$

where K and E are complete elliptic integrals of the first

* H. A. Schwarz, *Jour. f. Math.* (Crelle), vol. lxx. p. 115 (1869); *Ges. Abhandlungen*, vol. ii. p. 77.

and second kind to modulus $\sin \alpha$, and K' , E' those to modulus $\cos \alpha$. We find α by trial to make b/c correct, and then either equation determines C . Since $dz/d\xi$ tends to $-iC$ at infinity, $R=C$.

Let us apply the result to the circular ring of mean radius $a=1.735$ cm. and rectangular section 0.35 cm. by 0.33 cm., the inductance of which at 3250 metres was measured as 52.1 cm. We find $\alpha=44^\circ 13'$, $C=0.2005$. The high-frequency inductance is therefore, to a first approximation,

$$L=4\pi a \left(\log_e \frac{8a}{R} - 2 \right) = 48.77 \text{ cm.}$$

The low-frequency inductance, to the same order (Maxwell's formula) being 54.87 cm., there is a loss of 6.10 cm. from low to high frequency. The loss for a circular cross-section would be half the mean perimeter, or 5.46 cm., so that the estimated inductance of 51.0 cm. at 3250 metres may be too high by 0.3 cm. or so, whereby the agreement with experiment becomes slightly worse. It is satisfactory to find that the margin of theoretical uncertainty is quite small.

LXXVIII. *Critical Electron Energies in Helium, and the Extreme Ultra-Violet Spectrum.* By ANN CATHERINE DAVIES, D.Sc., Royal Holloway College, Englefield Green*.

IN a notice in 'Nature' of August 26th, 1922, Professor Lyman reported the detection of several hitherto unobserved lines in the extreme ultra-violet spectrum of helium. The lines in question were at 584.4 , 537.1 , 522.3 , and 515.7 , ÅU, correct to within one or two tenths of a unit, and a faint line at 600.5 ± 0.3 ÅU., and they were detected by maintaining a good vacuum in the body of the vacuum spectroscopie, while the discharge tube contained helium at about 1 mm. pressure. No separating window was used between the discharge tube and the spectroscopie, but a short narrow slit separated them and a powerful pump was kept in action. Previous to this the only helium line which had been detected in this region of the spectrum was $\lambda 585$, now given as 584.4 ÅU, and this had been observed by Fricke and Lyman†.

Of the lines referred to above $\lambda 584.4$ was found to be the most intense, and the intensities of the next three lines were

* Communicated by Prof. F. Horton.

† H. Fricke and T. Lyman, *Phil. Mag.* xli. p. 814 (1921).

found to decrease with their wave-length in a manner analogous to that found with successive lines of a series. Lyman points out that the frequency differences of the first four lines are identical with the frequency differences of the first four lines of the parhelium principal series of single lines given in Fowler's notation as $1S-mP$, and he considers that the ultra-violet lines detected form part of the principal series $0S-mP$, and that the ionization energy for electrons in helium must correspond to the limit of this series. Indicating the normal state by N , it seems probable that the first four lines given by Lyman belong to the series $N-mP$, in which case the ionization voltage should correspond to the limit of this series, N , which can be calculated accurately and should be, as Lyman has shown, equal to 24.5 volts. The calculation does not, however, involve the assumption that N is identical with the state $0S$.

The value of the ionization voltage calculated by Lyman in this way does not agree with the value which has been determined experimentally by Horton and Davies*, and by Franck and Knipping†, namely 25.2 volts, and the voltages corresponding to the lines observed by Lyman do not agree with the critical voltages which Franck and Knipping found intermediate to the fundamental resonance radiation voltages, and the ionization voltage. Lyman has, however, pointed out that a correction of -0.8 volt applied to all Franck and Knipping's values for helium would bring them into good agreement with the spectroscopic data, though it would leave the lowest critical voltage with no corresponding line in the ultra-violet spectrum.

In the experiments of Franck and Knipping‡, and also those of Horton and Davies§, the higher critical voltages have all been determined relatively to the first critical voltage, and the accuracy of the absolute values given depends, therefore, upon the accuracy of the determination of the absolute value of this first critical point. In the case of the determination made by Professor Horton and the writer, the fact that identical mean values were yielded by two methods with entirely different sources of possible error, one of which might give too high a value, and

* F. Horton and A. C. Davies, *Proc. Roy. Soc. A*, vol. xcv. p. 408 (1919), and *Phil. Mag.* vol. xlii. p. 746 (1921).

† J. Franck and P. Knipping, *Phys. Zeits.* vol. xx. p. 481 (1919), and *Zeits. f. Phys.* vol. i. p. 320 (1920).

‡ *Loc. cit.*

§ *Loc. cit.*, also F. Horton and A. C. Davies, *Phil. Mag.* vol. xxxix. p. 592 (1920); and A. C. Davies, *Proc. Roy. Soc. A*, vol. c. p. 599 (1922).

the other of which might give too low a value, was taken as indicating that the errors were negligible; the common mean value was therefore taken as the true absolute value of the first critical electron energy. For the details of the apparatus and the arrangements of electric fields employed in the two methods, the reader is referred to the original account of the experiments (Proc. Roy. Soc. A, vol. xcv. p. 408, 1919). Only the essential points will be given here.

The first method consisted in ascertaining the minimum value of the applied accelerating potential difference for which a photoelectric current due to the action of radiation on the collecting electrode could be detected, and applying to this minimum value a correction to allow for the velocity of emission of electrons from the filament, etc. The only possibility of error in the value deduced in this way is connected with the difficulty of ascertaining the appropriate correction to apply, because the special experiments made to investigate the initial energy of emission of the electrons showed that this quantity varied for different electrons over a range of about 2 volts. The determination of the minimum value of the applied potential difference at which the effects of radiation could be detected could be carried out with considerable accuracy, for the arrangement of electric fields was such as to prevent the collection of any of the original electrons, or any positive ions to which they might give rise by bombardment of the electrodes or by ionization of the gas, while, at the same time, it was such as to enable the accelerated electrons to traverse a considerable distance with their maximum energy at any applied potential difference before being retarded. It thus provided for the occurrence of collisions throughout a considerable region as soon as the applied accelerating potential difference reached a critical stage, thus causing the critical point to be well marked in the curve which showed the relation between the current measured by the electrometer and the applied accelerating potential difference.

The correction which was added to the value of the applied potential difference at the critical point, to give the energy of the electrons actually producing the effect detected, was the difference between the accelerating voltage, V_1 , and the subsequent retarding voltage, V_2 , when the number of electrons reaching the collecting electrode after traversing the opposing potential difference, V_2 , was the minimum number required to give a measurable current. Owing to the fact that in order to reach the collecting electrode the electrons had to pass through three gauzes, the number of

electrons collected was very much smaller than the number actually having energies $V_2 - V_1$ volts in excess of the applied accelerating potential differences. As the magnitude of the radiation current was probably somewhat similarly reduced by the intervening gauzes, the absolute value of the critical voltage deduced by the application of this maximum correction is nevertheless only likely to err on the side of being too high.

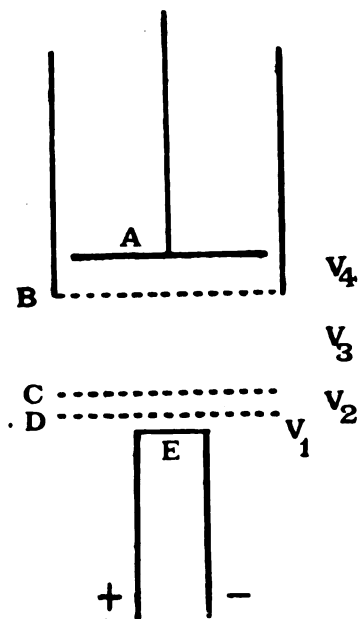
The results since obtained in an investigation of critical electron energies in neon *, by Professor Horton and the writer, have tended to confirm the view that the correction obtained in the manner described above is too large. In the investigation referred to, the correction was determined by controlling by means of a retarding potential difference, V_3 , the number of electrons which were allowed to pass into a space where they could acquire sufficient energy to make collisions of the type under investigation, and by finding the maximum value of V_2 which would allow of the passage of a sufficient number of electrons to give a detectable indication of the effects of the collisions in as nearly as possible the arrangement of fields employed in obtaining the curve for which the correction was required. The values of the positive correction obtained by subtracting V_1 , the first accelerating potential difference, from this value of V_2 , were generally smaller than the values obtained by a method similar to that used in helium, the difference in some cases amounting to a volt or so.

The second method of ascertaining the absolute value of the critical electron energy involved the detection of the occurrence of an inelastic collision, rather than the secondary effects of an inelastic collision. It did not involve the application of a correction for energy of emission from the filament, etc. The essential features of the method can be made clear by reference to the diagram in fig. 1, in which B, C, and D, represent gauzes of fine platinum wire, B forming the base of a hollow cylindrical electrode concentric with the collecting electrode A. E denotes the source of electrons. The electrons from E were accelerated towards the gauze D by a potential difference V_1 which remained constant, and those passing through this gauze were further accelerated by a potential difference V_2 which could be increased in steps of one-tenth of a volt. B and C were maintained at the same potential, and the pressure used (about 1 mm. or so) was sufficiently high for all the electrons to collide with helium atoms many times before reaching B.

* Proc. Roy. Soc. A, vol. xcvi. p. 124 (1920).

Between B and A an opposing potential difference V_4 was applied which could, like V_3 , be increased in steps of one-tenth of a volt. Below the first critical voltage electrons make perfectly elastic collisions with helium atoms. Consequently if V_4 is fixed at some value below the first critical voltage there must be a stage when, as V_3 is increased, electrons are able to reach the collecting electrode and give a negative current, whereas when V_4 is fixed at some value greater than the first critical voltage, inelastic collisions

Fig. 1.



must occur before the energy necessary to enable the electrons to reach the collecting electrode against V_4 is attained, and if *all* the electrons make inelastic collisions, electrons from E can then never reach the collecting electrode.

The method consisted, therefore, in ascertaining for various values of V_4 whether, as V_3 was increased, a negative current could be obtained at any stage, and hence determining the lowest value of V_4 for which no negative current could be measured as $V_1 + V_2$ was increased to beyond the first critical stage. When $V_1 + V_2$ exceeded a certain value

a positive current was always obtained, due presumably to the photoelectric effect of the radiation emitted at the critical stage on the collecting electrode. As the current always began to increase in the positive direction for the same value of $V_1 + V_2$, whatever the value of V_4 , the pressure must have been sufficiently high for all (or very nearly all) the electrons to have been making inelastic collisions. The lowest value of V_4 at which no indication of electrons reaching the collecting electrode was obtained, was taken as the first critical electron voltage. The extreme values of the critical electron energy measured in this way were 20.3 volts and 20.45 volts, the final mean value being 20.4 volts in agreement with the value obtained by the other method.

In taking the lowest value of V_4 at which there was no indication from the observations that electrons ever reached the collecting electrode, as the actual value of the first critical electron energy, it was assumed that there were no complications due to polarization layers on either of the electrodes bounding the final field. As, however, the effect of a polarization layer, if such existed, could only be to cause the measured potential difference to be smaller than the actually existing opposing potential difference, the result obtained in this way would, if it erred at all, be too low. Since the value obtained by the other method which, if it erred at all, would be too high, agreed with the value obtained by the method just described, the value 20.4 volts was taken to be the absolute value of the first critical electron energy.

The results of subsequent experiments* have revealed the existence of two critical radiation voltages in the neighbourhood of 20 volts in helium, 0.8 volt apart. It has, moreover, been shown by Professor Horton and the writer, that the radiation current due to the recovery of the atom after the inelastic collision at the higher of the two voltages is very much larger than that which appears at the lower energy collision. This is possibly due to the fact that collisions of the higher energy type occur more readily than those of the lower energy type, but there is no definite proof of this. This possibility, combined with the fact that the current due to the secondary effects of the inelastic collision of higher energy quantum is so much greater than the current caused by collisions of the first type, raises the question as to whether the minimum value of V_4 for which no indication of electrons reaching the collecting electrode

* J. Franck and P. Knipping, *Phys. Zeits.* vol. xx. p. 481 (1919); and F. Horton and A. C. Davies, *Phil. Mag.* vol. xlii. p. 746 (1921).

was obtained in the investigation described above, corresponds to the higher energy stage, or to the stage at which the first type of inelastic collision occurs. It is possible that at the first voltage of inelastic impact some of the electrons get over without making an inelastic collision, and that the negative current due to these electrons exceeds the positive current due to the photoelectric effect of the radiation produced from those inelastic collisions which do occur, thus masking the fact that such impacts have taken place. At the second critical stage, however, fewer electrons are likely to escape making inelastic collisions, and a much increased radiation current is produced, so that it is possible that the method just described indicated the true value of the second critical stage instead of the first, as was originally thought, in which case the value of 20.4 volts is 0.8 ± 0.1 volt too high for the true value of the first critical radiation voltage. As the other critical voltages determined in subsequent papers were measured relatively to the first one, a correction of the same amount must in this case be applied to them also. The correction necessary to bring the value of the ionization voltage determined experimentally into agreement with the value deduced by Professor Lyman is -0.7 volt.

In a recent paper * Franck has explained that an error of interpretation was involved in the method by which the fundamental absolute value of a critical voltage for electrons in helium was determined in Franck and Knipping's experiments. The error of interpretation in the case of their determination also was connected with the existence of the two critical energy stages 0.8 volt apart, so that the apparent difference of 0.8 volt between Lyman's calculated value and the experimentally determined value of the ionization voltage for electrons in helium, given by Franck and Knipping, is also explicable.

The bringing into alignment with the spectroscopic data of the values of the ionization voltage and some of the radiation voltages determined by other methods, does not, however, remove all the discrepancies between the results of the two lines of investigation. As has been pointed out by Lyman, there is no spectroscopic evidence of an ultra-violet line corresponding to the first radiation voltage (19.7 volts, after correction), while the faint line of doubtful origin at 600.5 ± 0.3 Å.U. is the only one which approximates to correspondence with the second and most marked radiation:

* J. Franck, *Zeits. f. Phys.* vol. ii. p. 155 (1922).

voltage found by Professor Horton and the writer at 20.5 volts (after correction).

If, as Lyman supposes, the normal state of the helium atom is the state $0S$, and his detection of a series with variable term mP suggests that this is the case, the presence of lines $N-1\sigma$ and $N-1S$, which would be those corresponding to the above-mentioned critical points, would not be in accordance with Bohr's selection principle, according to which only those transitions involving a change of one unit in the azimuthal quantum number take place*. Experiments described by Professor Horton and the writer in the *Philosophical Magazine* for November 1921, have shown, however, that the radiations emitted at 20.4 volts and 21.2 volts (*i. e.* 19.7 volts and 20.5 volts after correction) are true resonance radiations and should, therefore, be connected by the quantum relation $eV = h\nu$ with the critical voltages. These experiments seem to indicate that the transitions $N-1\sigma$ and $N-1S$ must have been occurring in the circumstances of the investigation referred to. As Franck and Knipping also obtained indisputable evidence of the emission of radiation previous to the stage which they now identify as corresponding with the emission of the line λ 584.4, and at a voltage which would correspond with the transition $N-1S$, it seems that the circumstances of their investigation, and also those of the investigation of Professor Horton and the writer, must have been such as to constitute an instance when the ordinary limitations of the selection principle did not hold, and when combination series lines could be obtained.

In a recent paper † Professor Bohr, in commenting on the results of an investigation by Foote, Mohler, and Meggers, on the excitation of the potassium arc spectrum ‡, pointed out that certain results which were thought by these workers to provide an exception to the selection principle, constituted, on the contrary, evidence in favour of that principle, because the very device which was employed in order to allow recombination to occur in the absence of an applied electric field would cause accumulations of ions from which intense electric fields would result. The main objection to applying arguments of a nature similar to those put forward by Professor Bohr to the present case, lies in the fact that it has been shown that the radiations emitted at 20.4 volts

* N. Bohr, *Phil. Mag.* vol. xliii. p. 1112 (1922).

† *Loc. cit.*

‡ P. D. Foote, F. L. Mohler, and W. F. Meggers, *Phil. Mag.* vol. xliii. p. 659 (1922).

and 21.2 volts (i. e. 19.7 volts and 20.5 volts after correction) can be passed on from atom to atom for a considerable distance by means of their absorption and re-emission by other helium atoms in regions where there could not possibly have been intense electric fields of the strength found by Stark* to be essential for the emission of the lines of the series $1S - mS$.

The displacement of an electron to the $1S$ orbit from the $0S$ orbit by electron collisions would not necessarily constitute a violation of the selection principle, for it is conceivable that the close proximity of the colliding electron and the impacted atom gives rise to the necessary strong electric field. A similar argument cannot, however, be applied to the return of the electron from the $1S$ to the $0S$ orbit, or to the displacement of the electron to the $1S$ orbit by the absorption of radiation. Thus the circumstances in which the radiations $N - 1\sigma$ and $N - 1S$ have been detected by Professor Horton and the writer seem to be such that a breaking down of the selection principle is necessarily indicated by their presence if $0S$ is the normal state; but whether N is identical with $0S$ or not, the fact that transitions $N - 1S$ and $N - 1P$ both occur must involve a breaking down of the selection principle.

Indirect evidence that the return of the displaced electron from the state $1S$ to the normal position takes place is provided by the following considerations:—The singlet principal series of helium $1S - mP$, which appears in the visible and near ultra-violet part of the spectrum, corresponds to transitions in which $1S$ is the orbit finally occupied by the moving electron, while in the case of the doublet principal series 1σ is the orbit finally occupied. Without the absorption of further energy the atoms can then only revert to the normal state by means of the direct transitions which would give the lines $N - 1S$ and $N - 1\sigma$, for there is no evidence of the transition $1S - 1\sigma$. Confining attention to the singlet system of lines, we see that, unless the transition $N - 1S$ does occur, there would be, on suddenly stopping a luminous discharge, an accumulation of atoms with electrons in the $1S$ orbits. Since the singlet principal series in the visible spectrum is comparable in intensity with the other series, the number of such abnormal atoms which would be present on stopping the discharge would be an appreciable proportion of the total number of atoms which were emitting radiation at any instant while the discharge was passing. Thus, after once having had an intense

* J. Stark, *Ann. d. Phys.* vol. lvi. p. 577 (1918).

luminous discharge in helium, it should be possible to obtain evidence of the occurrence of ionization on raising the potential difference from zero to about 5 volts, if the transition $N-1S$ does not occur. Such low-voltage ionization of helium does not, however, take place except when special measures are adopted to maintain a supply of abnormal atoms*, so that there seems no alternative to supposing that the transition $N-1S$ does occur.

The fact that this line was not clearly indicated in Professor Lyman's experiments is therefore worthy of consideration. An explanation of its absence is perhaps to be found by supposing that, although the selection principle does not hold rigorously as regards the transition $N-1S$, yet the transition is one which is not likely to take place when alternative displacements are possible. While a discharge is actually passing in the gas there is always the possibility of atoms with electrons in the $1S$ states absorbing radiant energy and ultimately reverting to the normal state from one of the P states, by the transitions of whose occurrence Lyman's results give evidence. Such methods of return from the $1S$ state to the normal state must have been possible in the circumstances of Professor Lyman's experiment, so that on the supposition made above, the line $N-1S$ would not be expected to occur with any great intensity on Professor Lyman's plates.

In the case of the experiments of Franck and Knipping, and of Professor Horton and the writer, however, abnormal atoms with electrons in the 1σ and $1S$ orbits could be produced before atoms with electrons in any of the P orbits could be produced. In the interval between the voltages at which the first two types of abnormal atom were produced, and that at which electrons could be removed to the $1P$ orbits, no radiant energy would be present unless the transitions $N-1\sigma$ or $N-1S$ occurred. Hence atoms with electrons in the 1σ and the $1S$ orbits would have no method of returning to the normal state, except by direct transitions, so that in these circumstances the radiations $N-1\sigma$ and $N-1S$ should be produced.

In view of the apparent discrepancies between the results of the spectroscopic and the current-voltage lines of investigation, a consideration of the extent to which current-voltage observations may be expected to reveal the existence of ultra-violet spectrum lines seems desirable. In what follows attention will be confined, for the sake of simplicity,

* F. Horton and A. C. Davies, *Phil. Mag.* vol. xliv. p. 1140 (1922); and F. M. Kannenstine, *Astro. Phys. Journ.* vol. lv. p. 345 (1922).

to the singlet system of helium. Taking the values of the critical radiation voltages corrected to fit Professor Lyman's spectroscopic observations, it has been shown that between 20.5 volts and 21.12 volts the transition $N-1S$ occurs, and the current-voltage curve indicates that $\frac{di}{de}$ increases when the electron energy reaches 20.5 volts, i being the photo-electric current and e the applied difference of potential. At 21.12 volts electron energy the displacement of an electron to the $1P$ orbit can result from an encounter between a helium atom and an electron. Experiments have shown, however, that for a given number of bombarding electrons the number of inelastic collisions which occur increases as the excess of energy of the electrons above the minimum energy required for the occurrence of the inelastic collision increases. It follows, therefore, that by no means all the electronic-atomic encounters involving the necessary minimum electron energy are effective in producing electron displacements within the atom. Suppose that the probability of the displacement of an electron within a helium atom to the $1S$ orbit at a 21.2 volts collision is p_1 and that the probability of a displacement to the $1P$ orbit at a 21.2 volts collision is p_2 . As the transitions in question are concerned with displacements from the normal orbit to orbits of different azimuthal quantum number, it is conceivable that the circumstances necessary for the occurrence of the one are quite distinct from the circumstances necessary for the occurrence of the other. In this case the probability that one or the other will occur at 21.2 volts is $p_1 + p_2$. The quantity $\frac{di}{de}$ would therefore be expected to show an increase as soon as the transition $N-1P$ was possible.

As the applied difference of potential is increased, stages are eventually reached at which transitions to orbits $2P$, $3P$, etc., or orbits $2S$, $3S$, etc., become possible. It is difficult to conceive how, apart from the minimum voltage consideration, the circumstances necessary for the transition to the $2S$ orbit to take place can differ from those necessary for a displacement to the $1S$ orbit, and so on, or, in the case of the P terms, how the circumstances necessary for a displacement to the $2P$ orbit can differ from those necessary for a displacement to the $1P$ orbit. Hence it appears that discontinuous increases in the number of inelastic collisions occurring would not be expected to take place at the voltages corresponding to the minimum electron energies necessary to

bring about displacements to the successive orbits of higher radial quantum number than the first of any series. Discontinuous changes in $\frac{di}{de}$ would therefore only occur at such voltages if the specific photoelectric activity of the surface acted upon by the radiation changed appreciably with wave-length in passing from $N-mS$ to $N-\overline{m}+1S$, or from $N-mP$ to $N-\overline{m}+1P$, and so on*. There is no direct experimental evidence available as regards the variation of photoelectric activity with wave-length of the radiation for the region 500 Å.U. to 600 Å.U., but such a variation as that considered is very unlikely.

The arguments given above have shown that whereas the current-voltage line of investigation may reasonably be expected to give an indication of the first terms of various series corresponding to transitions involving a return of the displaced electron to the normal orbit, it by no means follows that the method will give any indication of the existence of the higher members of these series. It seems doubtful, therefore, whether Franck's interpretation of a discontinuity at a point in his curves which, after correction, becomes 22.9 volts, as corresponding to the line $0.5S-3P$, or, in Fowler's notation, $0S-2P$, is justified.

Summary.

In view of the fact that there is a difference (9.7 volt) between the value of the ionization voltage for electrons in helium deduced from extreme ultra-violet spectroscopic observations by Professor Lyman, and the value obtained experimentally by Professor Horton and the writer, and independently by Franck and Knipping, the possible sources of experimental error, or error of interpretation of results, in the case of the determination made by Professor Horton and the writer are discussed.

It is shown that the discovery, made since the publication of the investigation in question, that there are *two* critical radiation voltages in the region of the first point of inelastic impact, separated by only 0.8 volt, introduces the possibility that an error of interpretation of the observed effects was made, resulting in values being attributed to all the critical

* For the lower members of these series, the fact that in passing from, for example, $N-1P$ to $N-2P$, returns to the normal orbit by the two transitions $N-1S$ and $1S-2P$ as an alternative to $N-2P$ become possible, does not mean an increase of photoelectrically active radiation, for the radiations such as $1S-2P$ would be of too long a wave-length to affect the platinum electrode.

voltages in helium which are too high by 0.8 volt $\pm$ a small experimental error.

Evidence is produced to show that the selection principle of Bohr, according to which only those transitions occur which involve a change of one unit in the azimuthal quantum number, cannot hold rigorously with regard to transitions to the normal state in helium. A possible explanation is given of the absence of certain lines which are indicated by the current-voltage observations, from Lyman's photographic plates, and the question of the ability of the current-voltage method to reveal the existence of ultra-violet series lines is discussed. It is concluded that whereas the method may reasonably be expected to indicate the first lines of series involving a return of the displaced electron to the normal orbit, it would probably not reveal the existence of the higher members of those series.

LXXIX. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 384.]

December 6th, 1922.—Prof. A. C. Seward, Sc.D., F.R.S., President and afterwards Mr. R. D. Oldham, Vice-President, in the Chair.

THE following communication was read:—

‘Geological Investigations in the Falkland Islands.’ By Herbert Arthur Baker, D.Sc., D.I.C., F.G.S.

The stratigraphical succession in the Falkland Islands comprises rocks of Archæan, Devono-Carboniferous, and Permo-Carboniferous age.

There is only one exposure of Archæan rocks in the Colony: namely, in the cliffs of Cape Meredith, the southernmost point of West Falkland. The rocks seen include various igneous types (pegmatite, granite, gneiss) and metamorphic rocks (hornblende-schist, quartzite). The pegmatite and schist are also invaded by lamprophyre-dykes.

Overlying these old rocks, and separated from them by a strong unconformity, are coarse sandstones and quartzitic rocks, nearly horizontal. This unfossiliferous series is of great thickness, probably about 5000 feet. It occupies the southern part of West Falkland as far north as Port Edgar and Port Richards, and also the islands lying to the west of this area. It is generally horizontal, or dips fairly gently northwards and eastwards. It is regarded as of Devonian age, and in its lithological characters shows remarkable similarity to the Table Mountain Series of the Cape Province, with which it is correlated.

The succeeding series of rocks of Devono-Carboniferous age occupy the remainder of West Falkland (except for small areas of

Permo-Carboniferous rocks) and the northern half of East Falkland, and comprise strata correlated with the Bokkeveld and succeeding Witteberg Series of the Cape Province, to which they are notably similar in lithological character. The typical marine molluscan and crustacean fauna of the Bokkeveld Series is yielded by the middle Devonian-Carboniferous series of the Falklands, and the succeeding beds are shales and quartzites, with poorly-preserved plant-remains, like the Witteberg Beds of the Cape of Good Hope. The Middle and Upper Series each include about 2500 feet of strata.

Terrestrial deposits of Permo-Carboniferous age follow. They occupy a synclinalorium extending over the whole of the southern half of East Falkland (Lafonia) and Falkland Sound. They also occur in small, separate areas on West Falkland. The name 'Lafonian Formation' has been given to this set of beds by Dr T. G. Halle. They include a thickness of strata exceeding 9000 feet.

As in the Southern Karroo, the lowest beds of this younger system are glacial boulder-beds. There is a tillite formation, about 2300 feet thick, in every way comparable with the Dwyka Tillite. Shaly beds occur locally between the boulder-beds and the older quartzite, but are often absent. There is a thin representative of the Upper Dwyka Shales of the Southern Karroo.

A sandstone formation (Lafonian Sandstone) of no great thickness follows, and is, in turn, succeeded by more than 6000 feet of terrestrial deposits. Several thousand feet of these Upper Lafonian Beds consist of a monotonous alternation of thin sandstones and shaly beds. They have yielded the *Glossopteris* Flora in several places. These upper beds appear to be the equivalent of the Ecce Series of the Southern Karroo. In view of their thickness, it is possible that some portion of the Beaufort Series of the Karroo System may be represented, but no evidence of this was obtained.

Doleritic dykes are of frequent occurrence. Their age is post-Upper Lafonian, since they are seen to cut the highest strata in the Colony.

With regard to the precise age of the marine Devonian fauna of the fossiliferous series of the older rocks, a difficulty arises. Palæontologists in general admit no more than that this fauna is of Devonian age. Some have insisted, however, that its age is Lower Devonian. The glacial boulder-beds at the base of the Permo-Carboniferous are now very generally regarded as of Upper Carboniferous age, and the Witteberg Beds of the Cape Province have recently been considered by Sir T. W. Edgeworth David as of highest Lower Carboniferous, and possibly, in part, Middle Carboniferous age. In the Cape Province and the Falkland Islands strata of Witteberg age can be traced downwards, without a break and without traversing an excessive thickness of strata, into the marine fossiliferous series. It seems likely that the marine fauna will prove to be of Upper Devonian age.

The Falkland Islands appear to owe their existence to the fact that they occur at the crossing-place of two sets of folding movements.

LXXX. *Intelligence and Miscellaneous Articles.*

ON THE FAILURE OF THE RECIPROCITY LAW IN PHOTOGRAPHY.

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

I REGRET that in my paper on the Failure of the Reciprocity Law in Photography (Nov. 1922, p. 904), there is an error on page 910. It is there stated that the mean values of the constant p and the probable errors are as follows:—

For Paget "Half-Tone" plates.....	$p = 0.865 \pm 0.005$
for Wratten "Instantaneous" plates ..	$p = 0.846 \pm 0.005$
for Imperial "Eclipse" plates	$p = 0.846 \pm 0.005$

This should read:—

Paget "Half-Tone"	$p = 0.865 \pm 0.058$
Wratten "Instantaneous".....	$p = 0.846 \pm 0.044$
Imperial "Eclipse"	$p = 0.846 \pm 0.052$

The probable errors, as printed, are therefore incorrect. The values of p are correct.

I greatly regret that this error in computation should have occurred.

The Laboratory,
British Museum,
39 Russell Sq., W.C. 1.
Jan. 23, 1923.

Yours faithfully,
R. A. MALLEY.

PRECESSION OF THE SPINNING TOP.

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

THE following additions should be made to my paper in the March number:—

Insert an * after the equation in the fifth line on page 387, and add the following as a footnote:—

To cut off OL geometrically on OG to a length

$$L = \frac{OP^2}{AP^2} OA,$$

draw EL through E on PA where the angle AEO is made equal to θ : OP is then tangent of the circle round OAE.

Yours faithfully,

March 13, 1923.

G. GREENHILL.

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

MAY 1923.

LXXXI. *The Quantum Theory and Isotopes.* By J. W. NICHOLSON, F.R.S., *Fellow of Balliol College, Oxford* *.

IN the present paper, we group together various matters which are of importance in regard to the Quantum theory of spectra and of atomic structure. No definite arrangement is followed, the subjects being very much disconnected. But they all appear to be somewhat insufficiently dealt with in current accounts of the Quantum theory, and to be capable of a treatment which can make them suggestive of further progress in directions along which experimental work is now proceeding.

Pendulum-paths in an Atom.

Pendulum-paths, or "Pendelbahnen," are frequently referred to, as particular cases, in discussions of atomic theory. They are straight-line paths of an electron in an atom or molecule. The intensity of a spectrum line emitted when an atom passes between two stationary states is determined by the probability of the occurrence of these states among a large number of other equally likely states. The probability of the repeated formation of a state in which any electron describes a "Pendelbahn" is effectively negligible, so that such states, in themselves, are never likely to be effective in producing visible spectrum lines.

* Communicated by the Author.

Phil. Mag. S. 6. Vol. 45. No. 269. May 1923.

3 F

But we know, from the familiar discussion by Sommerfeld and others of the fine structure of the Balmer series, that the "energy" W of an atom takes the same set of values, whatever system of coordinates be used in its calculation. The electronic orbits depend, even in their type, on the system of coordinates used—whether spherical polar or otherwise,—and yet all systems of orbits give the same total energy as a function of integer numbers, and thence, by the principles of Bohr's theory, the same spectrum.

This fact arises from the peculiar additive property of the Quantum integers, which ensues from the quantum specification of Wilson and Sommerfeld,

$$\int p \, dq = nh,$$

where q is any coordinate defining the system, p is the corresponding momentum, and the integration is taken over a complete period of q . The additive property involves, in particular, that, except for fine structure, the spectrum of a Hydrogen atom consists of the Balmer and its associated series, whether the electron be allowed all its possible three-dimensional motions, or merely the circular motions in one plane treated by the original theory of Bohr. This conclusion is quite general, in so far as the Quantum theory has hitherto been successful in its interpretation of spectral phenomena. The one outstanding fact on which reliance can be placed is apparently that the theory can give the significant part of the atomic energy, but is vague regarding the precise orbits of the electrons.

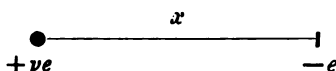
It has been suggested—for example, by Sommerfeld—that in any case there does exist, in fact, one and only one type of coordinate system which can lead to a solution when all the circumstances, such as variation of mass with speed, are taken into account, and that the orbits obtained according to this system are the true orbits. No evidence against this view can be found, and it is at least clear that the values of the "energy" W are not dependent on the system adopted. Moreover—and this is more relevant to our purpose at present,—the simplest possible orbits give the same value of W as those which are more complex in the analytical sense. It is therefore clear that the proper line of thought, with a view to extending the scope of the present theory, is to develop those cases which are analytically simple, with the knowledge that if the value of W is found, it will at least be a special case of the general value, in which more integers occur, and that it will, through the additive property of

integers when more degrees of freedom are contemplated, give spectrum lines which can be observed, though they may not in practice arise from atoms in which these simpler paths are relevant.

When the simpler paths are "Pendelbahnen," the preceding remarks apply, with the important addition that all the "true" paths must admit Pendulum-paths as special cases, so that values of W derived from them have a more complete validity. They constitute, in fact, the only paths about which there is any real certainty, either as to their nature or mode of description.

No complete investigation has yet been given of any one Pendulum-path. Sometimes they are ruled out because they involve a passage of the electron through the nucleus. On this matter we shall comment later, at present merely regarding such a passage as possible, and as involving neither an infinite velocity nor a destruction of matter by combination of electron and nucleus.

We shall discuss the simplest possible case—the Pendulum-path of a single electron about a nucleus—and show that, if the passage through the nucleus is a physical possibility, this path is indeed a special case which presents no infinite velocity or other difficulty of this nature. The electron will pass through the nucleus with the velocity of light (c), travelling in a straight line. We may treat the nucleus as stationary without real loss of generality, for its motion merely involves a change in the Rydberg Constant in the ordinary way.



If x is the distance of the electron from the nucleus ve at any instant,

$$m\ddot{x} = -\frac{ve^2}{x^2}$$

is the equation of motion when the velocity is small, and m is the mass of the electron at slow speeds. For higher velocities, attained in this problem, we use the relativistic mechanics, according to which the kinetic energy is, with velocity $\dot{x}$,

$$T = mc^2 \left\{ \frac{1}{\sqrt{1-\dot{x}^2/c^2}} - 1 \right\}.$$

and the equation of energy becomes

$$mc^2 \left\{ \frac{1}{\sqrt{1-\dot{x}^2/c^2}} - 1 \right\} - \frac{ve^2}{x} = -W,$$

W being the "total energy" in the Quantum theory sense.

The momentum $m\dot{x}$ is to be quantized according to

$$\oint m\dot{x} dx = nh,$$

where n is an integer. We find

$$1 - \frac{\dot{x}^2}{c^2} = m^2 c^4 / \left\{ mc^2 - W + \frac{ve^2}{x} \right\}^2.$$

When $x=0$, $\dot{x}=c$, which is therefore the velocity of passage through the nucleus. The oscillation takes place between the values of x making $\dot{x}=0$, or

$$m^2 c^4 = \left(mc^2 - W + \frac{ve^2}{x} \right)^2$$

leading to

$$-W + \frac{ve^2}{x} = 0, \quad -2mc^2,$$

or

$$x = \frac{ve^2}{W}, \quad -\frac{ve^2}{2mc^2 - W}.$$

These will be called $(\alpha, -\beta)$ respectively. Thus on reduction

$$\begin{aligned} m\dot{x} &= mc \left\{ \left(\frac{e^2 v}{x} + mc^2 - W \right)^2 - m^2 c^4 \right\}^{1/2} / \left(\frac{ve^2}{x} + mc^2 - W \right) \\ &= mc \left\{ \left(\frac{e^2}{v} - \frac{e^2}{\alpha} \right) \left(\frac{e^2}{x} + \frac{e^2}{\beta} \right) \right\}^{1/2} / \left\{ \frac{e^2}{x} + \frac{1}{2} e^2 \left(\frac{1}{\beta} - \frac{1}{\alpha} \right) \right\} \\ &= 2mc \sqrt{\alpha\beta} \cdot \sqrt{(\alpha-x)(\beta+x)} / \{ 2\alpha\beta + x(\alpha-\beta) \}. \end{aligned}$$

The quantizing condition becomes, since x ranges from α to $-\beta$ and back, in a complete period,

$$2 \int_{-\beta}^{\alpha} m\dot{x} dx = nh,$$

$$\text{or} \quad \frac{nh}{4mc \sqrt{\alpha\beta}} = \int_{-\beta}^{\alpha} \frac{dx}{2\alpha\beta + x(\alpha-\beta)} \cdot \sqrt{(\alpha-x)(\beta+x)}.$$

Writing

$$x = \alpha \cos^2 \phi - \beta \sin^2 \phi,$$

$$\begin{aligned} \frac{nh}{4mc \sqrt{\alpha\beta}} &= 2(\alpha + \beta)^2 \int_0^{\pi/2} \frac{\sin^2 \phi \cos^2 \phi d\phi}{2\alpha\beta + (\alpha - \beta)(\alpha \cos^2 \phi - \beta \sin^2 \phi)} \\ &= 2(\alpha + \beta) \int_0^{\pi/2} \frac{\sin^2 \phi \cos^2 \phi d\phi}{\alpha \cos^2 \phi + \beta \sin^2 \phi} \\ &= 2(\alpha + \beta) \int_0^\infty \frac{t^2 dt}{(\alpha + \beta t^2)(1 + t^2)^2}, \quad (t = \tan \phi). \end{aligned}$$

The integral is easily evaluated as $\frac{\pi}{4} (\sqrt{\alpha} + \sqrt{\beta})^{-2}$, so that

$$\frac{nh}{4mc \sqrt{\alpha\beta}} = \frac{\pi}{2} \frac{\alpha + \beta}{\alpha + \beta + 2 \sqrt{\alpha\beta}}.$$

But

$$\alpha + \beta = 2vmc^2 e^2 / \{W(2mc^2 - W)\},$$

$$\alpha\beta = v^2 e^4 / \{W(2mc^2 - W)\},$$

and finally,

$$\frac{nh}{2\pi mc} = ve^2 / \left\{ \sqrt{W(2mc^2 - W)} + \frac{W}{mc^2} (2mc^2 - W) \right\}.$$

This is the exact equation for W . If

$$W(2mc^2 - W) = X^2$$

we find

$$\frac{X^2}{mc^2} + X = \frac{2\pi vmce^2}{nh}.$$

and the general value of X , and thence W , can be expressed. For a first approximation only,

$$\frac{nh}{2\pi mc} = \frac{ve^2}{c \sqrt{2mW}}$$

or

$$W = \frac{2\pi^2 m e^4 v^2}{n^2 h^2},$$

which is the value belonging to other orbits, to a first approximation. It is easy to show that the result is correct to any approximation.

The ratio of the lengths of path before and after passage through the nucleus is

$$(2mc^2 - W) / W,$$

or effectively

$$\frac{n^2 h^2 c^2}{\pi^2 e^4 \nu^2};$$

with the values $h = 6.5 \times 10^{-27}$, $e = 4.8 \times 10^{-10}$, this becomes of order

$$\frac{n^2}{\nu^2} \times 10^6;$$

with a Hydrogen atom in its normal state, $n = \nu = 1$. If its radius is of order 10^{-9} , the electron, after passing the nucleus, goes a distance of order only 10^{-14} , less than its own radius, but comparatively large in relation to the "radius" of the nucleus.

This distance is so small, in comparison with orbital dimensions in an atom, as to justify the statement that, in effect, the electron does not traverse the core of the atom—though, in its small penetration, it reaches a point from which it can again reach the nucleus with velocity c and return to its former stationary position on the other side, subsequently continuing its oscillations. The time spent on the far side of the nucleus is also very small. We may conjecture, therefore, that the spectrum formula may be derived by ignoring, even in this case, the influence of speed on mass, and by supposing that the electron starts with $\dot{x} = 0$ and just reaches the nucleus and returns on its path. We shall show that this is, in fact, the case. While the investigation is not of intrinsic importance in the simple Pendulum problem of the Hydrogen atom as such, it has important implications with regard to the corresponding problems for more complex atoms. For it will be clear to the reader that the conclusions derived in this special case have general features. In the first place, when, in a Pendulum problem, an electron "goes through" a nucleus, it will do so with the velocity of light, and for a negligible distance in comparison with the rest of its path. Secondly, the problem may be treated as though the electron stopped at the nucleus. The simplification thus introduced is very considerable, and nothing is lost by these suppositions except the fine structure of the spectrum lines—a secondary consideration in the elucidation of the structure of atoms more complex than Hydrogen, or of molecules.

The simple pendulum problem for the Hydrogen atom with a stationary nucleus, and without correction for variable mass of the electron, gives for the equation of energy

$$\frac{1}{2}m\dot{x}^2 = \frac{e^2}{x} - W,$$

and the quantum condition is

$$\oint m\dot{x} dx = nh$$

or

$$2 \int_0^{e^2/W} m\dot{x} dx = nh$$

by the preceding remarks, according to which the nucleus $x=0$ is one end of the path. Thus

$$\frac{1}{2}nh = \sqrt{2m} \int_0^{e^2/W} \sqrt{\left(\frac{e^2}{x} - W\right)} dx.$$

Writing $x = \frac{e^2}{W} \sin^2 \theta$,

$$\begin{aligned} \frac{1}{2}nh &= \sqrt{2m} \int_0^{\pi/2} \sqrt{W} \cdot \frac{\cos \theta}{\sin \theta} \cdot \frac{2e^2}{W} \sin \theta \cos \theta d\theta \\ &= e^2 \sqrt{\frac{2m}{W}} \frac{\pi}{2}, \end{aligned}$$

or

$$W = \frac{2\pi^2 m e^4}{n^2 h^2},$$

which establishes the validity of the procedure. In general, in such paths, we may say further that the influence of the velocity on the mass is unimportant except for fine structure of the lines.

A few remarks on the penetration of the nucleus by an electron are perhaps desirable at this point. It is customary to speak of nucleus and electron as though they were, in a sense, hard lumps with a specific radius in each case, and capable of impact. As a convenient form of words, there is no objection to this, though it cannot approximate to the truth. If we reason in terms of an æther, the electron and nucleus are both states of strain in the æther, in some sense complementary, and any constants, such as charges and radii, associated with them, must be, in fact, constants of the possible strains which the æther can retain permanently — and therefore constants of the æther itself. As regards the

radius of an electron, for example, if the strain outside its centre follows a highly convergent law with distance r , it must be of the type $f\left(\frac{r}{a}\right)$, where a is a length—and this is essentially the so-called radius of the electron, or the distance at which the strain-intensity has fallen to a specific small value. Such considerations were advanced by the author several years ago, and the universality of the constants of electrons and nuclei is thereby referred back to a universality of structure in an æther, on a scale so small that its effect is only felt in phenomena which we relate to a single electron or nucleus.

In such circumstances, interpenetration of electric charges merely means the coexistence of two separate strains at the same place. A double-mesh structure in the æther, with different line constants (radius of electron and nucleus) in its specification, would admit this possibility, so that two strain systems in the same region would not annihilate each other, and might move through each other. The analysis of this section indicates how such problems may be treated very simply, with a sufficient practical approximation.

We shall leave the problem of Pendulum-paths at this point, reserving the investigation of the more complex systems for a further paper.

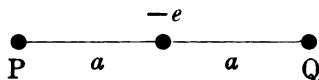
Nuclear Structure.

It is of interest to inquire into the implications inherent in the present view that nuclei have a structure built up from electrons and simpler nuclei—perhaps only the Hydrogen nucleus $+e$. This view is now practically general, and yet it is not without its difficulties. For if we consider even such simple systems of compound nuclei as, for example, a nucleus $2e$ and one electron, or the suggested Helium nucleus consisting of 4 Hydrogen nuclei and two electrons, it is very difficult to find an arrangement which restricts the total dimensions of the compound nucleus to any values comparable with the known dimensions.

It is almost unthinkable that the motions in these systems should not be subject to the quantizing principle, for their elements are “bound” in a still more intimate sense even than the external electrons of an atom. They can hardly be quantized by the introduction of a new quantum of action, different in order from h , and yet by the consideration of so simple a system as the suggested Helium atomic nucleus, it is easily seen that if the two electrons move in orbits in the

nucleus, the smallest possible orbits round the 4 Hydrogen nuclei are of atomic size. Either the law of force does, in fact, change—though experiments contradict this supposition—or the electrons are not in motion. The principle of coexistence already suggested may provide the only solution of these difficulties, but it is interesting to try, on more recognised lines, to obtain a nuclear representation.

We shall begin with a possible Hydrogen isotope—the so-called “inverted Bohr model” of Lenz, in which two nuclei rotate symmetrically round an electron. The structure seems very unstable, but the order of magnitude of the orbital radius must be the same as that in any more probable configuration, of this or of similar systems, in which the motion belongs to the nuclei.



If P and Q are the nuclei, $+e$, rotating with angular velocity ω in a circle of radius a ,

$$Ma^3\omega^2 = e^2(1 - \frac{1}{4}),$$

$$Ma^2\omega = \frac{\tau h}{2\pi},$$

whence the value of W is

$$W = \frac{2\pi^2 Me^4}{\tau^2 h^2} \cdot \frac{9}{16}.$$

If this system changed its quantum number, it would give radiations of the types— n being wave number,—

$$n = \frac{9}{16} \cdot \frac{M}{m} \cdot 109720 \left(\frac{1}{\tau_1^2} - \frac{1}{\tau_2^2} \right),$$

which fall in the region of X-rays. Such nuclear specifications, in general, are suitable, as regards order of magnitude of emitted wave-lengths, for the representation of characteristic X-ray radiation, provided that the orbital motions are those of nuclei of mass M. This correspondence of theoretical and experimental magnitude does not appear to have been pointed out.

The radius of the nucleus is given, from the above equations, by

$$a = \frac{4}{3} \frac{\tau^2 h^2}{4\pi^2 M e^2}$$

and the angular velocity by

$$\omega = \frac{9}{16} \frac{8\pi^2 M e^4}{h^3 \tau^3}.$$

If a_H is the "normal" radius of a Hydrogen atom,

$$a/a_H = \frac{4}{3} \cdot \frac{m\tau^2}{M} = 0.0007 \tau^2.$$

For $\tau=1$, the smallest nucleus, this is almost comparable with the radius of an electron, and gives a nucleus which is not definitely too large, within experimental error.

The velocity of a nucleus is

$$a\omega = \frac{3\pi}{2} \cdot \frac{e^2}{h\tau},$$

which, with the usual values of e and h , becomes

$$a\omega = \frac{1.6}{\tau} \times 10^{-6},$$

which is quite small in comparison with the velocity of light.

The value of ω , compared with that of the electron in a normal Hydrogen atom, is given by

$$\omega/\omega_H = \frac{9}{16} \cdot \frac{M}{m\tau^3} = \frac{10^3}{\tau^2},$$

so that this configuration, in its influence on an outer orbital electron making the atom neutral, can be treated as at rest in some mean position.

We propose to compare the spectrum of this neutral atom, which should be an isotope of Hydrogen, with that of Hydrogen itself—not because the atom may be presumed to exist, but because the order of magnitude of the spectral difference is clearly that to be expected in light isotopes of any type dependent on a nucleus built up of electrons and Hydrogen nuclei. At present there is complete uncertainty, on the theoretical side, as to the spectral difference to be looked for in any isotopes.

Spectra of Isotopes.

There are two sources of difference between the spectra of two isotopic forms of the same element, (1) the effect of a different mass in the nucleus, and (2) the effect of the distribution of nuclear charge, which does not produce a field, in the neighbourhood of the electron whose states define the spectrum, of the form appropriate to the point charge which is the core of a simple Hydrogen atom. We shall consider the orders of magnitude of (1) and (2).

The fact that the Rydberg constant N occurs simply in all ordinary arc series spectra is a somewhat conclusive proof that such spectra are due to an electron which is not much disturbed by the motions of other electrons, so that the rest of the atom acts upon this electron, to a first approximation, after the manner of a Hydrogen nucleus. For if two electrons were moving in outer orbits of approximately equal dimensions, this constant would be changed, as is easily seen, to $N(2-\frac{1}{4})^2$ in any good approximation to a spectral formula.

Consider an element of atomic weight M_σ —roughly σM_1 , where M_1 is the mass of a Hydrogen atom, for the mass is nearly all concentrated in the positive charges.

If one electron is more remote than the others, a series spectrum can be developed, in which the Rydberg constant is

$$N \frac{M_\sigma}{M_\sigma + m},$$

where m is the mass of an electron. This differs from the Hydrogen constant

$$N \frac{M_1}{M_1 + m}$$

by an amount roughly equal to

$$N \left\{ \frac{\sigma M_1}{\sigma M_1 + m} - \frac{M_1}{M_1 + m} \right\} = N \frac{(\sigma - 1) m}{\sigma} \frac{1}{M_1}.$$

Let the element now have an isotope, also of the same atomic number but with $\sigma + 1$ positive charges and an electron in its nucleus. Then the difference between the Rydberg constants of the two isotopes is

$$N \left\{ \frac{\sigma M_1}{\sigma M_1 + m} - \frac{(\sigma + 1) M_1}{(\sigma + 1) M_1 + m} \right\} = - \frac{m}{M_1} \cdot \frac{1}{\sigma(\sigma + 1)} N$$

to a sufficient approximation.

The proportional change in wave-length is effectively, in passing from one isotope to the other,

$$\frac{1}{\sigma(\sigma+1)} \frac{m}{M_1} \lambda,$$

where λ is the wave-length of any line.

For example, in Lithium, $\sigma=6$, for the lighter isotope needs 6 Hydrogen nuclei, and for the line $\lambda 6708$, the possible change is

$$\frac{6708}{6 \times 7 \times 1835} \text{ \AA} = 0.087 \text{ \AA}.$$

But in an element like lead, where $\sigma=200$ roughly, the change is only, in the region $\lambda 5000$, about

$$\frac{5000}{200 \times 201 \times 1835} \text{ \AA} = 0.00006.$$

The change from this source thus diminishes very rapidly down the periodic table.

The changes of this type which occur among the various lines of the same series should be proportional to their wave-lengths, to a sufficient practical approximation, for the effect is merely an alteration in the Rydberg constant.

It is clear that the effect to be expected in the Lithium atom, though comparatively large, is not comparable with that found by McLennan recently and ascribed to isotopes. Other interpretations have been put forward. The effect in Lead, however, is comparable with that actually known to occur (Merton).

We now consider the effect of the second type, due to the fact that the field of the nucleus and inner electrons is not that of a single point charge. In the case of the Hydrogen isotope, founded above on the inverted Bohr model, the nuclear radius is $a = 7\tau^2 \times 10^{-13}$ cm. approximately, and the angular velocity is

$$\omega = \frac{10^3}{\tau^2} \omega_H,$$

where ω_H is the value in a normal Hydrogen atom. Clearly the nuclear period is very much smaller, and the nuclear field on an electron may be replaced by its average value over one of its periods.

In the plane of the nuclear motion, the potential at time t ,

at distance r , is, with the notation in the figure,

$$\begin{aligned} V &= -\frac{e}{r} + \frac{e}{r_1} + \frac{e}{r_2} \\ &= -\frac{e}{r} + \frac{e}{\sqrt{r^2 + a^2 + 2ar \cos(\theta - \omega t)}} \\ &\quad + \frac{e}{\sqrt{r^2 + a^2 - 2ar \cos(\theta - \omega t)}} \\ &= -\frac{e}{r} + \frac{e}{r} \sum_0^{\infty} \frac{a^n}{r^{n+1}} P_n \{ \cos(\theta - \omega t) \} \{ 1 + (-1)^n \}. \end{aligned}$$

The mean value of any odd power of $\cos(\theta - \omega t)$ is zero. Thus

$$V = -\frac{e}{r} + \frac{2e}{r} \sum_0^{\infty} \frac{a^{2n}}{r^{2n}} P_{2n} \{ \cos(\theta - \omega t) \},$$

which gives, as mean value to order a^2 ,

$$V = -\frac{e}{r} + \frac{2e}{r} \left\{ 1 + \frac{a^2}{4r^2} \right\},$$

the mean value of $\cos^2(\theta - \omega t)$ being $\frac{1}{2}$.

Thus

$$V = \frac{e}{r} + \frac{ea^2}{2r^3}.$$

Just as Bohr's simple theory with circular orbits gave the essentials of the Hydrogen spectrum, so, with the present law of potential, the supposition of circular orbits saves much analysis and gives the main spectrum of the outer electron. If it moves in a circle of radius b with angular velocity ω ,

$$mb\omega^2 = e^2 \left(\frac{1}{b^3} + \frac{3}{2} \frac{a^2}{b^4} \right),$$

$$mb^2\omega = \frac{nh}{2\pi},$$

whence

$$b\omega = \frac{2\pi e^2}{nh} \left(1 + \frac{3}{2} \frac{a^2}{b^2} \right),$$

$$b = \frac{n^2 h^2}{4\pi^2 m e^2}$$

to the first order, and

$$W = \frac{2\pi^2 m e^4}{n^2 h^2} \left(1 + \frac{3a^2}{b^2} \right).$$

The Rydberg constant is changed by the fraction $3a^2/b^2$ of itself for the case $n=1$, and this is the greatest change, due to non-localization of the nuclear charge. With $b=5 \cdot 10^{-9}$, $a/b=0\cdot0007 \tau^2$, the change $\delta\lambda$ in a wave-length λ is given by

$$\frac{\delta\lambda}{\lambda} = 0\cdot05149 \tau^2,$$

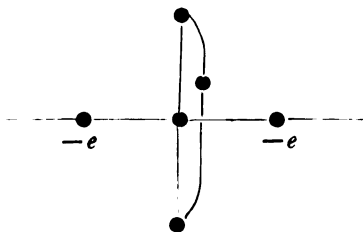
and for H_α , it would be

$$\delta\lambda = 0\cdot0098 \tau^2 \text{ \AA},$$

which could be detected if the isotope existed. The interest of the investigation lies, however, in the fact that this is the order of magnitude to be expected in isotopes of light atoms generally—and it is small in comparison with the other effect. The effect to be expected for Lithium is therefore of the order already specified.

More complex Nuclei.

The Helium nucleus now usually suggested consists of four Hydrogen nuclei or protons, and two electrons. The only simple arrangement they appear to admit, with the motion belonging only to nuclei, is shown in the figure.



The nuclei are equally spaced in a circular orbit, the electrons being on the axis. If $2a$ is the distance between the electrons, and b the radius of the orbit, we have

$$\frac{e^2}{4a^2} = \frac{4e^2a}{(a^2 + b^2)^{3/2}},$$

$$Mb^3\omega^2 = b^2 \left\{ \frac{2e^2b}{(a^2 + b^2)^{3/2}} - \frac{e^2}{b^2} \cdot \frac{1}{4} S_4 \right\},$$

where

$$S_4 = \operatorname{cosec} \frac{\pi}{4} + \operatorname{cosec} \frac{\pi}{2} + \operatorname{cosec} \frac{3\pi}{4} = 1 + 2\sqrt{2}.$$

Thus

$$b = a \sqrt{2^{8/3} - 1}, \quad \sqrt{a^2 + b^2} = 2^{4/3}a,$$

$$Mb^3\omega = e^2 \left\{ \frac{2^{8/3} - 1}{8} - \frac{1}{4} - \frac{1}{\sqrt{2}} \right\}$$

$$= 0.178e^2.$$

With a quantum of angular momentum at least for each nucleus,

$$Mb^3\omega = \frac{\tau\hbar}{2\pi}.$$

Thus

$$b\omega = 0.178 \frac{2\pi e^2}{\tau\hbar},$$

$$b = \frac{1}{0.178} \cdot \frac{\tau^2\hbar^2}{4\pi^2 Me^2},$$

and thence

$$a = \frac{(2^{8/3} - 1)^{-1/2}}{0.178} \frac{\tau^2\hbar^2}{4\pi^2 Me^2},$$

while the angular velocity is again so large that any external electron moves effectively in the "mean field" of the nucleus.

If a_H is again the normal radius of a Hydrogen atom, we find

$$\frac{a}{a_H} = 2.43 \frac{m}{M} \tau^2,$$

$$\frac{b}{a_H} = 5.62 \frac{m}{M} \tau^2.$$

The field of this nucleus, at a point on its axis, distant z from the centre, is

$$V = -\frac{e}{z+a} - \frac{e}{z-a} + \frac{4e}{\sqrt{z^2 + b^2}},$$

or, at a sufficient distance, compared with a or b ,

$$V = \frac{2e}{z} - \frac{2e}{z^3} (a^2 + b^2),$$

which, at any point (r, θ) in spherical polars, generalizes to

$$V = \frac{2e}{r} - \frac{2e}{r^3} (a^2 + b^2) \left(\frac{3 \cos^2 \theta - 1}{2} \right)$$

as the mean field of the nucleus.

This law of force does not admit a strictly circular orbit, but the occurrence of approximately circular orbits is possibly due to the smallness of the last term of V . If an approximate orbit is $r=c$, we may replace, for a sufficient first approximation, the last term by its mean value, thus writing

$$r = c, \quad \cos^2 \theta = \frac{1}{2}.$$

The equation of energy then becomes

$$\frac{1}{2} m(\dot{r}^2 + r^2 \dot{\theta}^2) - \frac{2e^2}{r} - \frac{2e^2}{c^3} \frac{(a^2 + b^2)}{4} = -W,$$

or

$$\frac{1}{2} m(\dot{r}^2 + r^2 \dot{\theta}^2) - \frac{2e^2}{r} = -W_1,$$

where $W_1 = W + \frac{2e^2}{4c^3} (a^2 + b^2)$.

This can be quantized in the ordinary way, the result being known to be

$$W_1 = \frac{8\pi^2 m e^4}{n^2 h^2},$$

where n is an integer. Moreover, for nucleus $2e$, the radius c becomes

$$c = \frac{n^2 h^2}{4\pi^2 m e^2}$$

to its first approximation, or mean value.

Accordingly,

$$\begin{aligned} W &= W_1 - \frac{2e^2}{4c^3} (a^2 + b^2) \\ &= \frac{8\pi^2 m e^4}{n^2 h^2} - \frac{8\pi^2 m e^4}{n^2 h^2} \cdot \frac{a^2 + b^2}{4c^2}. \end{aligned}$$

The proportional change in W due to nuclear distribution is therefore $(a^2 + b^2) / 4c^2$, and the corresponding change in any wave-length λ is given by

$$\frac{\delta\lambda}{\lambda} = \frac{a^2 + b^2}{4c^2},$$

due to change in its series limit.

If τ is the nuclear quantum number, by preceding results,

$$\frac{a}{a_H} = 2.43 \frac{m}{M} \tau^2, \quad \frac{b}{a_H} = 5.62 \frac{m}{M} \tau^2,$$

and c is the radius of the Helium atom with a double charge.

The normal value of this radius, corresponding to $n=1$, is $\frac{1}{4}$ that of the Hydrogen atom (a_H). For a quantum number n , the radius is proportional to n^2 . Thus the proportional change in the Helium line of wave number

$$4N \left\{ \frac{1}{p^2} - \frac{1}{q^2} \right\}$$

is

$$\frac{\delta\lambda}{\lambda} = 4 \{ (2.43)^2 + (5.62)^2 \} \left(\frac{m}{M} \right)^2 \tau^4 \left(\frac{1}{p^2} - \frac{1}{q^2} \right),$$

and, curiously, becomes proportional to λ^{-1} , so that $\delta\lambda$ is constant.

We find, on reduction,

$$\frac{\delta\lambda}{\lambda} = 0.0427 \tau^2 \left(\frac{1}{p^2} - \frac{1}{q^2} \right).$$

For example, the line $\lambda 4686$, for which $p=2$, $q=3$, gives

$$\begin{aligned} \delta\lambda &= 0.0427 \tau^2 \left(\frac{1}{2^2} - \frac{1}{3^2} \right) 4686 \\ &= 0.018 \tau^2 \end{aligned}$$

in Ångström units. The probable value of τ is unity, so that the change does not appreciably affect Fowler's calculation of m/M by comparison of the spectra of Hydrogen and of charged Helium.

But the correction for ionized Helium is much greater than for Hydrogen, and clearly it tends to increase as the atomic number of the element increases—so long as that atomic number is made up, in the nucleus, of a preponderance of protons or charged Hydrogen nuclei. It will clearly be very difficult to make up yet more complex nuclei in this way, with the experimental restrictions as to their dimensions, and as to the available law of force among their elements is concerned.

The general conclusion of this section, while not decisive, is certainly adverse to the hypothesis of nuclei made up entirely from Hydrogen. Perhaps our supposition that nuclear motions are subject to the quantizing relation is incorrect, though it is difficult to imagine, or to have faith in, any alternative.

We shall leave the matter at this point, with a view to a further communication.

December 27, 1922.

Phil. Mag. S. 6. Vol. 45. No. 269. May 1923.

3 G

LXXXII. *Some Approximations to Hypergeometric Functions.*
By DOROTHY M. WRINCH, D.Sc., *Fellow of Girton College,*
Cambridge, and Member of the Research Staff, University
College, London *.

THE importance of the Bessel functions

$$J_n(x) = \frac{(x/2)^n}{\Gamma(1+n)} \left\{ 1 - \frac{(x/2)^2}{1!(1+n)} + \frac{(x/2)^4}{2!(1+n)(2+n)} - \dots \right\}$$

$$I_n(x) = \frac{(x/2)^n}{\Gamma(1+n)} \left\{ 1 + \frac{(x/2)^2}{1!(1+n)} + \frac{(x/2)^4}{2!(1+n)(2+n)} + \dots \right\}$$

in mathematical physics has long been recognized. These functions are, however, particular cases of the hypergeometric function with s denominators †, which may be defined by the power series

$$1 + \frac{z}{1!(1+b_1)(1+b_2)\dots(1+b_{s-1})} + \frac{z^2}{2!(1+b_1)(2+b_1)(1+b_2)(2+b_2)\dots(1+b_{s-1})(2+b_{s-1})} + \dots$$

In the present paper, we are concerned with the hypergeometric function with four denominators

$$1 + \frac{z}{1!(1+b_1)(1+b_2)(1+b_3)} + \frac{z^2}{2!(1+b_1)(2+b_1)(1+b_2)(2+b_2)(1+b_3)(2+b_3)} + \dots, \quad (1)$$

when z is real and positive and when z is real and negative, and, further, with the hypergeometric function with five denominators and one numerator,

$$1 + \frac{(1+a)z}{1!(1+b_1)(1+b_2)(1+b_3)(1+b_4)} + \frac{(1+a)(2+a)z^2}{2!(1+b_1)(2+b_1)(1+b_2)(2+b_2)(1+b_3)(2+b_3)(2+b_4)(1+b_4)(2+b_4)} + \dots, \quad (2)$$

when z is real and positive and when z is real and negative.

* Communicated by the Author.

† Alternative methods of definition and certain properties of these functions are given in a forthcoming paper by the present writer.

The function (2) is evidently a particular case of the hypergeometric function with s denominators and t numerators,

$$1 + \frac{(1+a_1)(1+a_2)\dots(1+a_t)z}{1!(1+b_1)(1+b_2)\dots(1+b_s)} \\ + \frac{(1+a_1)(2+a_1)\dots(1+a_t)(2+a_t)z^2}{2!(1+b_1)(2+b_1)\dots(1+b_s)(2+b_s)} + \dots$$

The functions (1) and (2) have recently occurred in the problem of the lateral vibrations of bars of non-uniform cross-section*. In this problem the displacement is given in terms of the function

$$1 + \frac{x}{1!(1+b_1)(1+b_2)(1+b_3)} \\ + \frac{x^2}{2!(1+b_1)(2+b_1)(1+b_2)(2+b_2)(1+b_3)(2+b_3)} + \dots,$$

and the period equation takes the form

$$1 - \frac{(1+a)x}{1!(1+b_1)(1+b_2)(1+b_3)(1+b_4)} \\ + \frac{(1+a)(2+a)x^2}{2!(1+b_1)(2+b_1)\dots(1+b_4)(2+b_4)} - \dots = 0. \quad (3)$$

The present paper contains a simple approximation to the value of the functions (1), (2), when z is large and real and positive or large and real and negative, and an expression which gives to a high degree of accuracy the roots of the equation (3).

1.

1.1. It is known that for values of x which are real and positive, the asymptotic expansion for large values of x of the series

$$y_1 = \frac{1}{\Gamma(1+b_1)\Gamma(1+b_2)\Gamma(1+b_3)} \\ \left\{ 1 + \frac{(x/4)^4}{1!(1+b_1)(1+b_2)(1+b_3)} \right. \\ \left. + \frac{(x/4)^8}{2!(1+b_1)(2+b_1)(1+b_2)(2+b_2)(1+b_3)(2+b_3)} + \dots \right\}$$

* Cf. a paper by the present writer in the Proceedings of the Royal Society, A. vol. 101 (1922).

is given by

$$y_1 = \frac{e^{x(x/4)^{-\sigma}}}{2(2\pi)^{3/2}} \left\{ 1 + \frac{\alpha_1}{x} + \frac{\alpha_2}{x^2} + O\left(\frac{1}{x^3}\right) \right\},$$

where

$$\sigma = b_1 + b_2 + b_3 + 3/2$$

and α_1 and α_2 are certain functions of b_1, b_2 , and b_3 . Further, the series

$$y_2 = \frac{\Gamma(1+\gamma)}{\Gamma(1+b_1)\Gamma(1+b_2)\Gamma(1+b_3)\Gamma(1+b_4)} \left\{ 1 + \frac{(1+\gamma)(x/4)^4}{1!(1+b_1)(1+b_2)(1+b_3)(1+b_4)} + \dots \right\},$$

which reduces to y_1 in the special case when $\gamma = b_4$, has the asymptotic expansion

$$y_2 = \frac{e^{x(x/4)^{-\tau}}}{2(2\pi)^{3/2}} \left\{ 1 + \frac{\delta_1}{x} + \frac{\delta_2}{x^2} + O\left(\frac{1}{x^3}\right) \right\},$$

when x is real, positive, and large. In this expression

$$\tau = b_1 + b_2 + b_3 + b_4 - \gamma + 3/2$$

and δ_1, δ_2 are certain functions of b_1, b_2, b_3, b_4 , and γ .

1.2. To find the values of δ_1, δ_2 , which will, of course, yield the values of α_1, α_2 if b_4 be put equal to γ , we remark that y_2 satisfies the linear differential equation of the fifth order

$$\mathfrak{S}(\mathfrak{S} + 4b_1)(\mathfrak{S} + 4b_2)(\mathfrak{S} + 4b_3)(\mathfrak{S} + 4b_4)y_2 = x^4(\mathfrak{S} + 4 + 4\gamma)y_2.$$

If

$$y_2 = e^x x^{-\tau} y,$$

it follows that

$$\mathfrak{S}y_2 = e^x x^{-\tau}(\mathfrak{S} + x - \tau)y,$$

and the equation for y consequently becomes

$$(x - \beta_1 + \mathfrak{S})(x - \beta_2 + \mathfrak{S})(x - \beta_3 + \mathfrak{S})(x - \beta_4 + \mathfrak{S})(x - \beta_5 + \mathfrak{S})y = x^4(x - \sigma + 4 + 4\gamma + \mathfrak{S})y,$$

if we write

$$\beta_r = -\tau + 4b_r, \quad (r=1, 2, 3, 4),$$

$$\beta_5 = -\tau.$$

The left side of this equation is evidently of the form

$$y(x^5 + {}_1a_1x^4 + {}_1a_2x^3 + \dots) + \mathfrak{S}y(5x^4 + {}_2a_1x^3 + {}_2a_2x^2 + \dots) + \mathfrak{S}^2y(10x^2 + \dots) + \mathfrak{S}^3y(10x^2 + \dots) + \mathfrak{S}^4y(5x + \dots) + \mathfrak{S}^5y.$$

Now consider the expression

$$\prod_{r=1}^n (x - \beta_r + \S)y ;$$

it is evidently of the form

$$y(x^n + {}_1a_1x^{n-1} + {}_1a_2x^{n-2} + \dots) + \S y(nx^{n-1} + {}_2a_1x^{n-2} + \dots) + \dots + \S^n y.$$

We can obtain by induction the value of the $({}_ra_s)$ coefficients. In particular,

$$\begin{aligned} {}_1a_2 &= \Sigma_2 + \frac{(n-1)(n-2)}{2} \Sigma_1 + \frac{n(n-1)(n-2)(3n-5)}{24}, \\ {}_1a_3 &= \Sigma_3 + \frac{(n-2)(n-3)}{2} \Sigma_2 + \frac{(n-1)(n-2)(n-3)(3n-8)}{24} \Sigma_1 \\ &\quad + \sum_{s=1}^n \frac{(s-1)(s-2)(s-3)^2(3s-8)}{24}, \end{aligned}$$

where Σ_r represents the products r at a time of the n quantities $\beta_1, \beta_2, \dots, \beta_n$. In the particular case under discussion, $n=5$, and we have

$$\begin{aligned} {}_1a_2 &= \Sigma_2 + 6\Sigma_1 + 25, \\ {}_1a_3 &= \Sigma_3 + 3\Sigma_2 + 7\Sigma_1 + 15, \\ {}_2a_2 &= 4\Sigma_1 + 30, \end{aligned}$$

where Σ_r represents the sum of the products r at a time of the five quantities

$$-\tau + 4b_1, \quad -\tau + 4b_2, \quad -\tau + 4b_3, \quad -\tau + 4b_4, \quad -\tau.$$

1.3. The equation for y may conveniently be written in the form

$$\begin{aligned} y\{({}_1a_1 - 4 + 4\gamma - \tau).x^4 + {}_1a_2 + x^3 + \dots\} \\ + \S y\{4x^4 + {}_2a_1.x^3 + \dots\} + \dots = 0. \end{aligned}$$

Solving for y in series, we may put

$$y = 1 + \frac{\delta_1}{x} + \frac{\delta_2}{x^2} + \dots$$

Equating to zero the coefficient of the term of highest power in x , namely, x^4 , we obtain the result

$${}_1a_1 - (4 + 4\gamma - \tau) = 0.$$

The equation for y is now

$$y({}_1a_2x^2 + {}_1a_3x^3 + \dots) + Sy(4x^3 + {}_2a_2x^2 + \dots) + \dots = 0,$$

and equating to zero the terms in x^3 , x^2 , and so on, we get the series of equations

$$\begin{aligned} {}_1a_2 - 4\delta_1 &= 0, \\ {}_1a_3 + \delta_1 \cdot {}_1a_2 + 8\delta_2 - \delta_2 \cdot {}_2a_2 &= 0, \\ &\dots\dots\dots \end{aligned}$$

yielding the results

$$\begin{aligned} \delta_1 &= \frac{{}_1a_2}{4} = \frac{1}{4}(\Sigma_2 + 6\Sigma_1 + 25), \\ 8\delta_2 &= \delta_1({}_2a_2 - {}_1a_2) - {}_1a_3, \\ &= -\delta_1(\Sigma_2 + 2\Sigma_1 - 20) - (\Sigma_3 + 3\Sigma_2 + 7\Sigma_1 + 15). \end{aligned}$$

Succeeding equations will yield the value of the succeeding coefficients $\delta_3, \delta_4, \dots$. With the values of δ_1, δ_2 obtained above, we therefore have the approximation to the value of y_2 in the form

$$y_2 = \frac{e^x}{2(2\pi)^{3/2}} \left(\frac{x}{4}\right)^{-\tau} \left\{ 1 + \frac{\delta_1}{x} + \frac{\delta_2}{x^2} + O\left(\frac{1}{x^3}\right) \right\}.$$

1.4. We may write down a similar result for the function y_1 .

$$y_1 = \frac{e^x(x/4)^{-\sigma}}{2(2\pi)^{3/2}} \left\{ 1 + \frac{\alpha_1}{x} + \frac{\alpha_2}{x^2} + O\left(\frac{1}{x^3}\right) \right\},$$

where

$$\begin{aligned} \sigma &= b_1 + b_2 + b_3 + 3/2, \\ \alpha_1 &= \frac{1}{4}(\Sigma_2' + 3\Sigma_1' + 7), \\ 8\alpha_2 &= -\alpha_1(\Sigma_2' + 1) + \Sigma_3' + \Sigma_2' + \Sigma_1' + 1, \end{aligned}$$

Σ_r' representing the sum of the products r at a time of the four quantities

$$4b_1 - \sigma, \quad 4b_2 - \sigma, \quad 4b_3 - \sigma, \quad -\sigma^*.$$

This result may be obtained *ab initio* by obtaining the differential equation for y where

$$y_1 = e^x x^{-\sigma} y$$

* For convenience in actual computation, it may be remarked that $\Sigma_1' = 0$, in virtue of the relation between σ and b_1, b_2, b_3 .

and solving in a series

$$y = 1 + \frac{\alpha_1}{x} + \frac{\alpha_2}{x^2} + \dots,$$

or, more conveniently, by writing $b_4 = \gamma$ in the result obtained above for the series y_3 .

1.5. The series

$$y_3 = \frac{1}{\Gamma(1+b_1)\Gamma(1+b_2)\Gamma(1+b_3)} \left\{ 1 - \frac{(x/4)^4}{1!(1+b_1)(1+b_2)(1+b_3)} + \frac{(x/4)^8}{2!(1+b_1)(2+b_1)(1+b_2)(2+b_2)(1+b_3)(2+b_3)} - \dots \right\}$$

$$y_4 = \frac{\Gamma(1+\gamma)}{\Gamma(1+b_1)\Gamma(1+b_2)\Gamma(1+b_3)\Gamma(1+b_4)} \left\{ 1 - \frac{(1+\gamma)(x/4)^4}{1!(1+b_1)(1+b_2)(1+b_3)(1+b_4)} + \frac{(1+\gamma)(2+\gamma)(x/4)^8}{2!(1+b_1)(2+b_1)(1+b_2)(2+b_2)(1+b_3)(2+b_3)(1+b_4)(2+b_4)} - \dots \right\}$$

may be treated on similar lines. We will deal first with the series y_4 . Now, if x is real, positive, and large,

$$y_4 = \frac{e^{\frac{x \cos \frac{\pi}{4}}{(2\pi)^{3/2}} (x/4)^{-\tau}}}{(2\pi)^{3/2}} \left\{ \cos \left(x \sin \frac{\pi}{4} - \frac{\pi \tau}{4} \right) + \frac{\delta_1}{x} \cos \left(x \sin \frac{\pi}{4} - \frac{\pi(\tau+1)}{4} \right) + \frac{\delta_2}{x^2} \cos \left(x \sin \frac{\pi}{4} - \frac{\pi(\tau+2)}{4} \right) + O\left(\frac{1}{x^3}\right) \right\},$$

where, as before,

$$\tau = b_1 + b_2 + b_3 + b_4 - \gamma + 3/2,$$

$$\delta_1 = \frac{1}{4}(\Sigma_2 + 6\Sigma_1 + 25),$$

$$8\delta_2 = -\delta_1(\Sigma_2 + 2\Sigma_1 - 20) - (\Sigma_3 + 3\Sigma_2 + 7\Sigma_1 + 15)$$

Similarly,

$$y_3 = e^{x \cos \frac{\pi}{4}} (x/4)^{-\sigma} \left\{ \cos \left(x \sin \frac{\pi}{4} - \frac{\pi \sigma}{4} \right) \right. \\ + \frac{\alpha_1}{x} \cos \left(x \sin \frac{\pi}{4} - \frac{\pi(\sigma+1)}{4} \right) \\ \left. + \frac{\alpha_2}{x^2} \cos \left(x \sin \frac{\pi}{4} - \frac{\pi(\sigma+2)}{4} \right) + O\left(\frac{1}{x^3}\right) \right\}$$

and

$$\sigma = b_1 + b_2 + b_3 + 3/2,$$

$$\alpha_1 = \frac{1}{4}(\Sigma_2' + 3\Sigma_1' + 7),$$

$$8\alpha_2 = -\alpha_1(\Sigma_2' + 1) + (\Sigma_3' + \Sigma_2' + \Sigma_1' + 1).$$

The results given above enable us to estimate the value of y_1 , y_2 , y_3 , and y_4 in a simple manner, by the calculation of the coefficients α_1 , α_2 , δ_1 , δ_2 . The error in adopting these approximations is of relative order $\frac{1}{x^3}$, which is sufficient in the case of many practical applications.

2.

2.1. In order to obtain an approximation to the roots of an equation of the type

$$y_4 = 0,$$

we may adopt the approximation to the value of y_4 when x is large, which was obtained above. We therefore consider the roots of the equation

$$\cos \left(x \sin \frac{\pi}{4} - \frac{\pi \tau}{4} \right) + \frac{\alpha_1}{x} \cos \left(x \sin \frac{\pi}{4} - \frac{\pi(\tau+1)}{4} \right) \\ + \frac{\alpha_2}{x^2} \cos \left(x \sin \frac{\pi}{4} - \frac{\pi(\tau+2)}{4} \right) = 0.$$

If we put

$$\frac{\pi \tau}{4} + (s - \frac{1}{2}) \pi = \lambda_s,$$

we may write the equation

$$\sin\left(x \sin \frac{\pi}{4} - \lambda_s\right) + \frac{\alpha_1}{x} \sin\left(x \sin \frac{\pi}{4} - \lambda_s - \frac{\pi}{4}\right) + \frac{\alpha_2}{x} \sin\left(x \sin \frac{\pi}{4} - \lambda_s - \frac{\pi}{2}\right) = 0.$$

A first approximation when x is large is evidently

$$x \sin \frac{\pi}{4} = \lambda_s.$$

Then, putting

$$x \sin \frac{\pi}{4} - \lambda_s = \epsilon_s,$$

the equation is

$$\sin \epsilon_s + \frac{\alpha_1}{x} \sin\left(\epsilon_s - \frac{\pi}{4}\right) + \frac{\alpha_2}{x^2} \sin\left(\epsilon_s - \frac{\pi}{2}\right) = 0,$$

and we obtain the result

$$\left(1 + \frac{\alpha_1}{x\sqrt{2}}\right) \sin \epsilon_s = \left(\frac{\alpha_1}{x\sqrt{2}} + \frac{\alpha_2}{x^2}\right) \cos \epsilon_s.$$

If $1/\lambda_s^3$ and ϵ_s^3 be neglected, this becomes

$$\left(1 + \frac{\alpha_1}{2(\lambda_s + \epsilon_s)}\right) \sin \epsilon_s = \left(\frac{\alpha_1}{2(\lambda_s + \epsilon_s)} - \frac{\alpha_2}{2(\lambda_s + \epsilon_s)^2}\right) \cos \epsilon_s,$$

which yields the result

$$\epsilon_s = \frac{\alpha_1}{2\lambda_s} - \frac{\alpha_1^2}{4\lambda_s^2} - \frac{\alpha_2}{2\lambda_s^2}.$$

Thus, to the order $1/\lambda_s^2$, the roots of the equation $y_4 = 0$ are given by

$$x \sin \frac{\pi}{4} = \lambda_s + \frac{\alpha_1}{2\lambda_s} - \frac{\alpha_1^2 + 2\alpha_2}{4\lambda_s^2},$$

with

$$\lambda_s = \frac{\pi\tau}{4} + (s - \frac{1}{2})\pi.$$

2.2. We may calculate the roots given by this approximation in a particular case. Let

$$y_4 = \frac{1}{\Gamma 3 \Gamma 3\frac{1}{2} \Gamma 4} \left\{ 1 - \frac{(x/2)^4}{2 \cdot 4 \cdot 5 \cdot 6} + \frac{(x'/2)^8}{2 \cdot 4 \cdot 5 \cdot 6 \cdot 4 \cdot 6 \cdot 7 \cdot 8} \dots \right\}:$$

it is known that this series is a multiple of the function

$$\left\{ J_2\left(x \sin \frac{\pi}{4}\right) I_3\left(x \sin \frac{\pi}{4}\right) + I_2\left(x \sin \frac{\pi}{4}\right) J_3\left(x \sin \frac{\pi}{4}\right) \right\} / x^5,$$

where J_2, J_3, I_2, I_3 are Bessel functions.

The roots of the equation

$$y_4 = 0$$

are then given by the approximation

$$x \sin \frac{\pi}{4} = \lambda_s + \frac{\alpha_1}{2\lambda_s}$$

to the order $1/\lambda_s^2$, where

$$\tau = b_1 + b_2 + b_3 + b_4 - \gamma = 3/2,$$

$$\lambda_s = \frac{\pi}{4} \tau + (s - \frac{1}{2}) \pi,$$

the values of the parameters being in this case given by

$$b_1, b_2, b_3 = 1, 3/2, 2 : b_4 = \gamma.$$

Thus, in this case

$$\tau = 6, \quad \lambda_s = (s + 1) \pi.$$

Further,

$$\Sigma_1 = -10, \quad \Sigma_2 = 20,$$

so that

$$\alpha_1 = \frac{1}{4}(\Sigma_2 + 6\Sigma_1 + 25) = -\frac{15}{4}.$$

Therefore, neglecting terms of order $1/\lambda_s^2$, we have

$$x \sin \frac{\pi}{4} = (s + 1) \pi - \frac{15}{8\pi(s + 1)}.$$

The first nine roots of the equation

$$J_2(y) I_3(y) + I_2(y) J_3(y) = 0$$

are known. The values of y which satisfy this equation are

evidently the values of $x \sin \frac{\pi}{4}$, which satisfy the equation

$y_4 = 0$ in this particular case. Thus, the fact that the first nine roots are known offers a way of testing the approxima-

tion for the values of $x \sin \frac{\pi}{4}$ which satisfy the equation

$y_4 = 0$ which has been given above. We exhibit the two sets of values in the appended table.

$$x \sin \frac{\pi}{4}.$$

s.	Exact Value*.	Approximation.	Difference.
1	1·8807	1·9050	·0143
2	2·9275	2·9367	·0092
3	3·9478	3·9525	·0047
4	4·9591	4·9620	·0029
5	5·9660	5·9683	·0023
6	6·9714	6·9729	·0015
7	7·9751	7·9763	·0012
8	8·9781	8·9789	·0008
9	9·9804	9·9810	·0006

It appears, then, that the first two terms of the approximation give all the roots ($s=1, 2 \dots$) with an error of less than 2 per cent., and all the roots after the ninth with an error of less than ·06 per cent.

LXXXIII. *Emission and Absorption of Halogens in the Visible and Ultra-violet Regions.* By A. L. NARAYAN, M.A., A.Inst.P., and D. GUNNAYYA, B.A.†

[Plate XI.]

COLOURED gases and vapours are remarkable for the complexity of the banded spectra they give by absorption at low temperatures. Of these, the absorption exerted by the halogens is specially interesting, as their emission and absorption spectra are not complementary. The subject was studied by Hasselberg, Morre, Liveing and Dewar, Friederichs, &c., more recent work on the subject being by Evans on the absorption of Bromine and Iodine at different temperatures (*Astrophysical Journal*, xxxii. p. 1, 1910), and by M. Kimura and M. Fukuda (*Science Abstracts*, Section A, p. 436, 1921) on the emission of Chlorine.

The following experiments were therefore undertaken with the object of studying the emission and absorption spectra of these vapours in the visible and ultra-violet, and the effect of pressure on the absorption.

* Cf. J. R. Airey, *Proceedings of the Physical Society of London*, vol. xxii. p. 227 (1911).

† Communicated by the Authors.

Before the Mathematics and Physics Section of the Indian Science Congress, held in Madras recently, the authors read a paper containing some of these experiments. This paper contains a full account of those and other experiments we have since performed on these vapours.

The methods employed in this work for studying the effect of pressure on absorption are similar to those adopted by H. Jones and Anderson in their extensive investigations on the absorption spectra of solutions, viz. (1) to keep the pressure of the vapour constant and to vary the depth of the absorption cell; (2) to keep the depth constant and vary the pressure, i.e. concentration; (3) to vary both, thickness and pressure, of the absorbing layer in such a way that their product remains the same.

For absorption in the visible region, a Hilger glass spectrograph with a constant-deviation prism is used, eye observations being made with a Hilger direct-vision spectroscope. For work in the ultra-violet region, a Hilger quartz spectrograph provided with a wave-length scale is used, in which the whole region from 0.2μ to 0.78μ can be obtained in one exposure on a plate 10 inches long. In all these cases the absorption cells are glass tubes of different lengths furnished with two side tubulures against the ends, and the ends are closed with plane plates of glass or quartz by means of sealing-wax. In the case of bromine and iodine, tubes of 20 to 25 cm. in length were used, but in the case of chlorine, as the selective absorption in the yellowish-green region could not be seen with the above length, we had to use tubes of about a metre in length.

In photographing the spectra, Schumann plates made by Adam Hilger, London, and Wratten & Wainwright panchromatic "A" were used.

Source of Light.—For work in the visible region we used in some experiments a carbon arc, and in some others sunlight, as in this case the Fraunhofer lines serve as reference lines; and for work in the ultra-violet we used iron arc with some inductance and resistance in series, as the spectrum of iron is very rich in ultra-violet radiations, and the lines in the ultra-violet are so closely set that they almost form a continuous spectrum.

The emission spectra were examined both by Geissler tubes and by special discharge-tubes of about 20 to 30 cm. in length, 1 to 1.5 cm. in diameter, and furnished with two side tubes containing freshly prepared pure and well-dried silver halides, just sufficient to cover the platinum electrodes sealed through the tubes, the discharge-tube being connected

by means of a side tubulure to an exhaustion pump; and for discharge a 10-inch Apps induction-coil with an electrolytic interruptor and a condenser in parallel was used.

The emission spectra of bromine and chlorine are line spectra, the nature of which depends on the intensity of discharge and the temperature of the tube. As the intensity was increased, some lines were reinforced and others disappeared. As can be seen from fig. 4 (Pl. XI.), showing the emission spectrum of bromine in the visible region, it is not the strongest lines that are reinforced and that persist in the spectrum when the discharge is increased. The same was found to be the case with chlorine.

When we were investigating absorption of light by these vapours at low temperatures, there appeared the work of Sir J. J. Dobbie and J. J. Fox in the Science Abstracts, who studied the absorption of light by these gases at temperatures from 20 to 1350° C. As they used a Nernst filament lamp as the source of light, it was not possible for them to go beyond 3100 A.U.; and we thought it desirable to continue our experiments to study the absorption at different temperatures by using the iron arc as the source of light, as it would take us to 2000 A.U., which can be conveniently examined by the quartz spectrograph we used in the first series of experiments; and as will be seen from the photographs of the absorption spectra, this has led us to some interesting results.

Absorption Spectra.—All these vapours give a banded spectrum in the yellowish-green region between 5800 and 5000 A.U., the bands being sharp on the violet side and fading away towards the red end; and at the same time general absorption begins at the ultra-violet end and extends up to 4900 A.U. as the pressure of the gas is increased. With the increase of pressure the bands become darker, and a few more are added against the red end. In fact, these need not be considered to be new additions, but those that were previously very faint and are now reinforced on increasing the pressure. As can be clearly seen from the spectrograms, the general absorption band extends more and more with the increase of the pressure until at great pressures it extends up to the green, where the banded spectrum begins. If we compare figs. 5, 7, & 9 (Pl. XI.), showing the ultra-violet principal absorption bands, it would seem that this band shifts towards the less refrangible side with increase of atomic weight.

In making a spectrogram, a number of exposures were taken on a single plate with the vapour at different pressures,

and another exposure with the source of light alone to serve as comparison spectrum.

As for the dependence of absorption on temperature of the vapour, it will be seen that the absorption of bromine gradually increases from 30 to about 600°C ., at which it absorbs almost the whole of the ultra-violet up to 2000 A.U.; and after this again the absorption falls, and it becomes more and more transparent to ultra-violet radiations. The middle of the absorption band is not therefore situated at about 4170 A.U., as was thought by Dobbie and Fox. Further, the temperature of the maximum absorption according to our experiments is nearly 600°C . In the case of chlorine, the absorption increases slightly towards the red end with rise of temperature, but towards the short wave-length side there is no change at all, as it is clearly seen from the photographs, maximum temperature in our experiments being 800°C . nearly. In the case of iodine, absorption increases with temperature up to 300° nearly, and at 300° the ultra-violet up to 3250 A.U. is completely absorbed, and above this temperature the vapour again transmits the ultra-violet radiation.

Explanation of Plate XI.

- | | | |
|---|-------------------------------|--|
| Fig. 1. Absorption of Chlorine. | } In the visible region. | |
| 2. " " Bromine. | | |
| 3. " " Iodine. | | |
| 4. Emission spectrum of Bromine. | | |
| 5. Absorption of Chlorine at ordinary temperatures but for different pressures. | } In the ultra-violet region. | |
| 6. " " Chlorine at different temperatures. | | |
| 7. " " Bromine at ordinary temperature but for different pressures. | | |
| 8. " " Bromine at different temperatures. | | |
| 9. " " Iodine at ordinary temperatures but for different pressures. | | |
| 10. " " Iodine at different temperatures. | | |

It will be seen from these that with the greatest quantity of chlorine, absorption at ordinary temperatures did not extend above 2750 A.U., and in the case of bromine beyond 3450 A.U., while in the case of iodine it did not extend beyond 4100 A.U. The fact that the emission and absorption spectra of these vapours are not complementary might be due to different complexities of molecular structure of the vapours in the two cases. Further, Beer's law does not seem to hold good in the case of these vapours.

We are now investigating the absorption of these vapours in the infra-red region, the results of which will be published on completion of the work.

Department of Physics,
Maharajah's College, Vizianagram.

LXXXIV. *Absorption of Potassium Vapour.* By
A. L. NARAYAN, M.A., A.Inst.P., and D. GUNNAYYA, B.A.*

[Plate XII.]

RECENT experiments of McLennan and Young on the absorption of light by the non-luminous vapours of Zinc, Cadmium, &c., have shown that our knowledge of the structure of molecules may be increased by a study of the optical properties of the vapours of the various elements at low temperatures; for, as Prof. McLennan remarked in the Guthrie Lecture on the Origin of Spectra, March 22, 1918, for the elements for which the principal series $\gamma = (1.5 S) - (mP)$, it is found that the wave-lengths of this series are strongly absorbed by their non-luminous vapours. And it is beyond doubt that there is a profound and intrinsic link between absorption and dispersion and the structure of the molecule of an element. A careful study of the optical and magneto-optical properties, especially absorption and dispersion of vapours of the elements, will be a most important step towards the exploration of the intimate structure of the molecule.

A very complete study of the optical and magneto-optical properties of sodium vapour was made by Prof. Wood, in which the periodicities of the vibrating mechanisms were studied in a variety of ways by absorption and by powerful stimulation of the vapour with white and monochromatic light. Investigation of the absorption spectrum of sodium vapour (Phil. Mag. 1908 & 1909) by Prof. Wood raised the number of members of the principal series from the seven previously known to 48, the largest number absorbed for any element thus far; and the late Dr. P. V. Bevan applied Wood's method to the other alkali metals, and observed extended Balmer series in Li, K, Rb, Cs (Proc. Phys. Soc. 1909; Proc. Roy. Soc. 1910 & 1911). It will be seen that the number of members of the principal series in potassium was raised to 26, considerably less than the number in the other alkali metals. In view of the similarity between the absorption spectra of the different alkali metals, it was thought very desirable first to extend to the non-luminous potassium vapour, studies along the same line. The following investigation was therefore undertaken to study the absorption of potassium vapour at different temperatures.

The apparatus consists, as shown in the photographic reproduction (Pl. XII. fig. 6), of a thin seamless steel tubing

* Communicated by the Authors.

about 30 inches long and about 1 inch in diameter. The tube was furnished with two water boxes against the end s, and two small lateral tubes were brazed into the steel wall, one at each end, for connexion with the Fluess pump and gas generator. The ends were closed with two quartz plates, cemented to the tube with best sealing-wax. The whole tube was mounted in a metal frame on a stand provided with levelling screws, so that the tube could be conveniently placed with its axis parallel to that of the collimator of the spectrograph. With the exception of a length of about 4 in. in the middle, the portion of the tube between the water boxes was covered with heating-coils kept red-hot during the experiment; and a continuous flow of cold water was maintained through the water boxes throughout the experiment.

A pretty large quantity of the fresh metal was cut into strips and introduced into the middle of the tube. Then, by connecting the tube to a gas generator, dry hydrogen gas was passed through the tube for some time, and thus the potassium was kept in a hydrogen atmosphere. With the metal in the centre of the tube and the heating-coils at the ends raised to redness, rapid distillation of the metal to the colder parts and the consequent deposition on the quartz windows could be prevented, and exposures of any length could be made under quite steady conditions.

In these experiments carbon arc was used as the source of light, since some of the lines in the arc spectrum serve as reference lines. The tube being mounted in position, light from the arc was concentrated by a quartz lens at the centre of the steel tube, and after emergence it was focussed by another quartz lens on the slit of the spectrograph. First, the current in the heating-coils was started, and 10 minutes after that the tube was heated at the centre by the flame of a Tecluc burner, which gave a high temperature. When the tube was heated first, the absorption lines at the red end made their appearance, and as the temperature was raised the accompanying channelled spectrum developed. With the increase of temperature and the consequent increase of the density of the vapour the higher members of the Balmer series also developed. When the temperature and density of the vapour were sufficiently high to bring out the higher members of the series, it was found that the first two or three pairs of this series were immersed, so to speak, in a band spectrum, which was nothing but the accompanying channel spectrum subsequently developed into a dark band; and it was found by the authors that enormous increase in the

vapour-density was necessary to elicit the higher members of the series, the temperature of the tube being between 750° and 800° C. With the tube at this high temperature and with exposures of $1\frac{1}{2}$ to 2 hours, the Balmer series could be extended to 30, and still higher temperatures were found to be of no avail; but when the temperature was raised still further to about 950° C., the highest we could command in the experiment, some slight traces of absorption in the first members of the diffuse series were suspected; and it is not possible to say anything definitely about the absorption of this series as, we are now continuing our experiments in that direction.

Balmer Series.

In the following table are given the wave-lengths of the principal series lines we observed from $m=11$ to $m=29$, together with the values of Dr. Bevan. In another column we have given the values calculated from the formulæ :

$$\text{O.F.} = 35005.56 - \frac{109675}{\left\{ m + .293076 - \frac{.061356}{m-1} \right\}^2},$$

$$\text{O.F.} = 35005.56 - \frac{109675}{\left\{ m + .296228 - \frac{.061628}{m-1} \right\}^2}.$$

Independent measurements of the lines beyond the 20th were made by three different observers separately by means of a comparator made by C. S. I. Co., and on subsequent comparisons the maximum difference between our observations amounted to .1 A.U.

No. <i>m</i> .	Authors.	Bevan.	Calculated.
11	2928.10	2928.00	2927.86
12	2916.45	2916.6	2916.38
13	2907.6	2907.6	2907.45
14	2900.00	2900.4	2900.38
15	2894.5	2894.6	2894.67
16	2889.85	2889.7	2890.00
17	2886.2	2885.9	2886.1
18	2883.00	2882.9	2882.8
19	2880.4	2880.3	2880.12
20	2878.00	2877.9	2877.8
21	2875.7	2875.8	2875.8
22	2874.15	2874.1	2873.99
23	2872.3	2872.5	2872.46
24	2871.2	2871.1	2871.12
25	2870.0	2870.0	2869.9
26	2869.1	...	2868.89
27	2868.15	...	2868.0
28	2867.4	...	2867.2
29	2866.7	...	2866.45

In the red channelled spectrum the wave-lengths of about 15 bands were measured by a Hilger wave-length spectrometer, and all the bands are clearly seen on the photographic reproduction and its enlargement. This spectrum was studied by Roscoe and Schuster (*Proc. Roy. Soc. xxii. p. 362*), and by Wood and Carter (*Phys. Review, xxvii. p. 113, 1908*). The wave-lengths of the bands as measured by us are given in the following table. (For photographing the spectra we used Schumann plates and Wratten & Wainwright Allochrome plates, specially sensitive to actinic radiations.)

The red channelled spectrum.

No.	Wave-length.	No.	Wave-length.
1	6811.0	9	6488.5
2	6760.0	10	6443.0
3	6711.0	11	6412.0
4	6661.0	12	6388.8
5	6622.0	13	6366.1
6	6584.0	14	6332.2 (not
7	6544.1		clearly seen in
8	6506.0		the photograph).

Explanation of Plate XII.

- Fig. 1. Principal series lines for gradually increasing densities.
 2. " " " with greatest vapour-density; Temp. of tube = 100° C.
 3. Enlarged photograph of a portion of No. 2.
 4. Absorption in the visible region, showing the gradual development of the red channelled spectrum and its subsequent change to a dark band.
 5. Enlarged photograph of the same channelled spectrum, showing the 14 bands observed.
 6. Apparatus, etc.

In conclusion, we wish to express our best thanks to Mr. G. Subrahmanyam, B.A., of the Physics Department, for the very valuable assistance he has given during the progress of the work.

Department of Physics,
Maharajah's College, Vizianagram.

LXXXV. *On the Aeration of Quiescent Columns of Distilled Water and of Solutions of Sodium Chloride.* By Professor W. E. ADENEY, A.R.C.Sc.I., D.Sc., F.I.C., Dr. A. G. G. LEONARD, F.R.C.Sc.I., B.Sc., F.I.C., and A. RICHARDSON, A.R.C.Sc.I., A.I.C.*

Introductory.

IN the course of his investigations on the downward transmission of atmospheric gases through quiescent columns of water five feet in depth, one of the authors showed that, as the oxygen and nitrogen are dissolved at the exposed surface of the water, they do not remain concentrated in the surface layer, but are distributed through the lower layers with comparative rapidity.

From the fact that the distribution of the dissolved gases, at various depths, after a comparatively short time was almost uniform, it appeared impossible to account for it on the assumption that it was entirely due to such an extremely slow process as that of the diffusion of the dissolved gases from the saturated surface layer.

In addition to diffusion, it was suggested that a process of downward "streaming" of the exposed layer of water occurs; and that it results largely, though possibly not wholly, from an increase in its density, which, in the case of distilled water, is caused by the lowering of temperature attending evaporation, and, in the case of salt solutions, by this factor and that of concentration.

The downward streaming sets up a process of mixing of the constantly changing air-saturated surface layer with the lower layers of the water. When a slow stream of dry air is continuously passed over the exposed layer of a column of water, surface density changes are constantly occurring, and comparatively rapid mixing ensues, with the result that, if the water be de-aerated at the commencement of the experiment, it becomes re-aerated with comparative rapidity †.

The experiments described in this investigation have been carried out with the object of investigating the process of the aeration of de-aerated columns of water to a depth of ten feet. Columns of de-aerated distilled water and of solutions of sodium chloride were exposed to a slow stream

* Communicated by the Authors. Reprinted from the Proceedings of the Royal Dublin Society, vol. xvii. (n.s.).

† "Unrecognized Factors in the Transmission of Gases through Water." By W. E. Adeney, Trans. R. D. S. p. 161, 1905; and Phil. Mag. March 1905.

of dry air for periods of from two to eight weeks, when samples at different depths were drawn off, and the nitrogen content of each determined.

In general, it was found that re-aeration proceeded more rapidly in salt solutions than in pure water*, and a further series of experiments was carried out with solutions of sodium chloride, having a wide range of concentration, to ascertain the effect of concentration of the sodium chloride on the rate of aeration.

Experimental.

The de-aeration of the water employed in these experiments was effected by distillation *in vacuo*. In order to obtain water quite free from atmospheric gases, the distillation was at first carried on in a very slow current of hydrogen or of carbon dioxide; but, although the resulting water was air-free, it was always found to contain undesirable traces of hydrogen or of carbon dioxide, according to which gas was employed during the distillation. It was consequently decided to rely upon distillation under the reduced pressure obtained with the aid of a good water vacuum pump, employing a slow current of air, filtered through glass wool, to overcome difficulties from "bumping." The nitrogen content of the de-aerated water obtained did not exceed 1 c.c. per litre, which, in the case of pure water, amounts to about 7 per cent. of saturation at 15° C.

It was found unnecessary to determine the nitrogen content of each sample of water at the commencement of each aeration experiment, as it was found to be practically constant immediately after the de-aeration.

The glass tubes used in the experiments were about 3 cms. in diameter, and varied from 9 to 12 feet in length. T-pieces were fused on, at regular intervals, along the length of the tube, for drawing off samples of the water columns at different levels, and the lower ends of the tubes were sealed. The upper end of the tube was closed by a rubber stopper, fitted with an inlet and outlet tube, by means of which connexions were made to the pump and distilling apparatus; so that the water could be distilled directly into the experimental tube when desired.

In the case of salt solutions, the required quantity of sodium chloride was placed in a five-litre flask, connected with the vacuum distilling apparatus by means of a thick-wall rubber tube, and the required volume of pure water was allowed to distil into the flask and dissolve the salt, the

* See above references.

exact concentration of the solution being subsequently determined by analysis. A screw clip was then used to close the connexion with the pump, the flask detached with its rubber connecting tube, and attached, with the aid of the same connecting tube, to the experimental tube. When the free end of this connecting tube was completely filled with freshly distilled water, it could be attached air-free to the previously exhausted experimental tube. After attaching the flask to the tube, the latter could be filled by inverting the flask and unscrewing the clip, when the solution flowed into the tube.

Experimental tubes were also employed, which were furnished with quill capillary tubes, instead of side tubes, for drawing off samples. These tubes passed upwards through a rubber stopper at the bottom of the experimental tube to different levels inside, the external ends being attached each to a piece of thick-walled rubber tubing closed by a screw clip.

Each experimental tube was attached to a stout lath of wood for facility of removal from one laboratory to another. The room in which the aeration was carried out was one which received no direct sunshine nor heat from artificial sources, so that the temperature prevailing in it was not subject to sudden fluctuations. In the earlier experiments, a zinc cylinder, 14 inches in diameter and filled with water, was used as a jacket for the tubes. But it was subsequently found that a good wrapping of asbestos cloth was a sufficient guard against sudden variation in temperature. Manipulative difficulties were thereby considerably reduced, and it was possible to work with a greater number of tubes simultaneously.

A recording thermometer was kept in the room, and the greatest variation in temperature in the room, during the exposure of any one tube, did not exceed $4^{\circ}5\text{ C}$. This variation, however, was exceedingly slow—too slow to give rise to convection currents.

The air passing over the surface of the water in the tubes was first dried by calcium chloride; and the inlet tube was so arranged that the air did not play directly on to the surface. The inlet and outlet tubes were fixed at a distance of 1.5 to 2 inches above the water. The moist air issuing from the tube was passed through weighed CaCl_2 tubes, so that the amount of water evaporated could be determined for each tube. In most of the experiments three tubes were connected in series, drying-tubes being placed so that the moist air from one was dried before entering the succeeding tube.

A filter pump, worked by a constant head of water, seven

feet in height, was at first employed to aspirate the current of air through the tubes, but subsequently, owing to shortage of the town water supply, caused by the drought last summer, a different arrangement had to be substituted. An electrically driven small air pump was utilized to force air into a large glass vessel, which acted as an equalizer, and thence through the drying vessels and experimental tubes. This arrangement worked very satisfactorily.

The experimental tubes, having been filled with de-aerated water, were fixed in a vertical position; the stoppers, which had been used during filling, were removed, and were replaced by others carrying inlet and outlet tubes for the air current. The air current was continued for two or three weeks in the case of salt solutions, and three to eight weeks for pure water. The apparatus employed for the determination of the dissolved gases was of the form devised by one of the authors*.

*Method of withdrawing Samples from
the Experimental Tubes.*

Samples of water were withdrawn from an experimental tube, without at any time allowing them to come into contact with the air, with the aid of a modification of the gas burette used for the analysis of the dissolved gases.

By lowering the mercury reservoir, attached to the burette, a known volume of water was drawn from the tube into the latter, and thence transferred to a Plimpton gas holder to await examination. The depth from which the sample was drawn and the temperature of the water were at the same time noted. 50 c.c. of water were usually taken for the extraction and analysis of the dissolved gases in the case of the surface layer; and 100 c.c. for samples drawn from lower levels.

*Determination of Saturation Values for Nitrogen
of Sodium Chloride Solutions.*

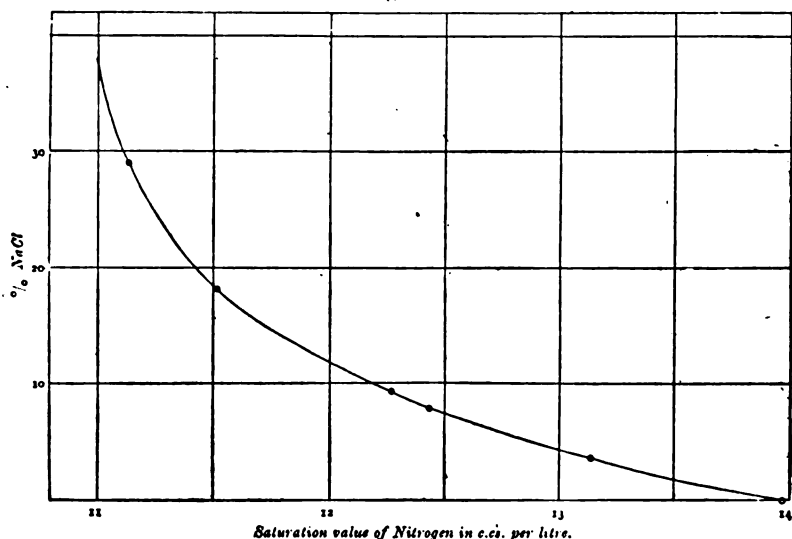
In order to calculate in percentages of saturation the observed rates of solution of atmospheric nitrogen by solutions of sodium chloride of the various concentrations employed in this investigation, it was necessary to determine the saturation values for atmospheric nitrogen of each solution. This was done by filling large tubes, about 5 cms. in diameter and 30 cms. in length, about two-thirds full of the salt solution. A current of air, previously passed through a glass

* Sci. Trans. R. D. S. vol. v. series 11, p. 548; also Supplemental vol. vi., Fifth Report of the Royal Commission on Sewage Disposal, p. 99.

wool filter and through distilled water to saturate it with aqueous vapour, was drawn through the solution under examination. The inlet tube reached to the bottom of the solution; and the apparatus was immersed in a thermostat. The current of air was continued for a sufficient time to ensure equilibrium being reached throughout the tube at the observed temperature. The dissolved nitrogen and the sodium chloride in the solution were then estimated.

The experimental results are shown by the accompanying curve (fig. 1).

Fig. 1.



Saturation values of Nitrogen in solutions of varying NaCl concentration at 15° C.

Method of expressing Experimental Results for the Purpose of Comparison.

The columns of water employed in these experiments were so deep—about ten feet—and the exposure of them to the air had to be continued over such extended periods of time—two to eight weeks—that it was decided not to attempt to control the temperature obtaining during the conduct of the experiments beyond preserving the room in which they were carried out, and which was exceptionally well circumstanced for such purpose, at as closely uniform temperature as possible during a set of experiments.

To have provided the means for controlling, at will, the temperature at which these experiments could be started and

continued would have added very considerably to the practical difficulties of an already sufficiently laborious problem; and it was not thought necessary to attempt to do so, since the authors had good reasons, which will be explained later on, for assuming that when the gas concentrations of a de-aerated column of distilled water, or of a solution of a salt, at any time during re-aeration were expressed in percentages of saturation, they would be found to increase practically in the same proportions at different temperatures, provided that the variation in temperature did not exceed 3° or 4° C.

This view was based upon the following considerations:—

(1) Dittmar has determined the saturation values of distilled and of sea-water for atmospheric nitrogen and oxygen between 4° C. and 35° C.; and when his results are plotted against temperatures, the curves obtained approximate to parallel straight lines between the limits 8° C. and 35° C.*.

(2) Adeney and Becker, in their work on the rate of solution of these atmospheric gases by distilled and by sea water, found that, when the experimental observations from zero to saturation were expressed as percentages of saturation and plotted against time, the curves obtained were coincident when uniform conditions of exposure of water to the gas, of the mixing of the exposed with the unexposed portions of the water, and of temperature (within 1° C.) obtained †.

It may be assumed from this that the curves showing the rate of solution of atmospheric nitrogen and oxygen by dilutions of sea-water with varying proportions of distilled water would also be coincident with the curves showing the same for distilled and sea-water, separately, under like conditions of exposure to air, of mixing, and of temperature varying within 1° C.

(3) Adeney and Becker further found that the curves showing the rate of solution in water of nitrogen and of oxygen, when stated in percentages of saturation, lie very closely together for differences of 5° C. within the range of temperature from 0° C. to 30° C.

Consequently it is possible to convert approximately, by simple calculation, observations made at slightly different temperatures, to those that would obtain at a selected common temperature, varying even to as much as 2 or 3 degrees from them, and still obtain sufficiently accurate results for purposes of comparison.

* Supplementary vol. vi. to the Fifth Report, Royal Commission on Sewage Disposal, p. 59.

† "The Determination of the Rate of Solution of Atmospheric Nitrogen and Oxygen by Water." By W. E. Adeney and H. G. Becker, Part 1, Sci. Proc. R. D. S. 1918, and Phil. Mag. April 1920, p. 385.

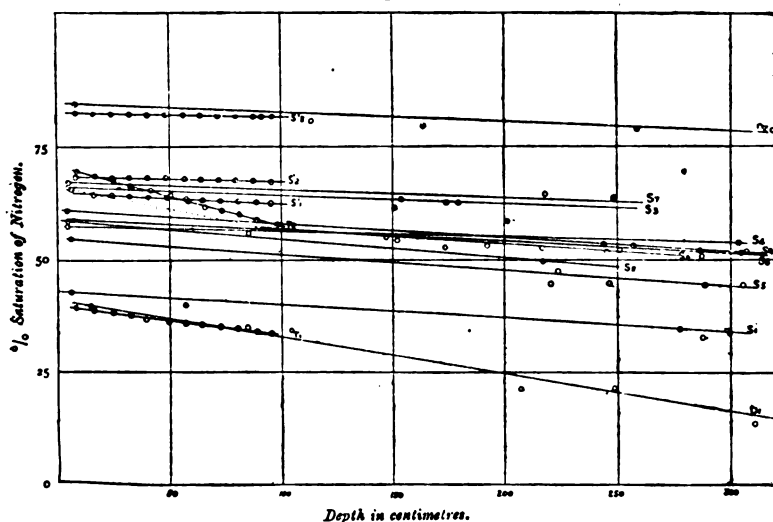
Experimental Results.

The conditions obtaining in some experiments with columns of salt solutions and of distilled water are given in the table on page 842.

Curves showing the nitrogen content of columns of distilled water, and of salt solutions, at different depths, expressed as percentages of saturation, are given in fig. 2.

On comparing the curves D_1 for distilled water (exposed to the air for twenty-seven days) and S_1 , for a 3.3 per cent.

Fig. 2.



Nitrogen content expressed in percentages of saturation at different depths below the surface.

salt solution (fourteen days), the effect of the salt on the progress of aeration is well illustrated. The curve for the distilled water column shows a fall in nitrogen content from 40 per cent. at the surface to 13 per cent. at a depth of 311 cms., whereas the corresponding values for the 3.3 per cent. salt solution ranged from 42.7 to 38.3 per cent. respectively in about half the time.

Even with a solution containing only 0.0116 per cent. sodium chloride (curve S_9), the effect of the salt in solution is well marked.

The curves S_1' , S_2' , S_3' , T_1 , and T_2 are plotted from results

	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	D_1	D_2
Initial concn. of N. in c.c. per litre	0.9	0.632	0.432	0.632	0.618	0.618	0.618	0.618	0.618	1.06	0.618
Initial concn. of N. as percentage of saturation }	8.85	6.22	5.17	5.08	4.74	4.66	4.36	4.76	4.74	6.92	4.65
Percentage of NaCl	3.343	1.97	0.94	0.41	0.25	0.116	0.008	0.629	0.0116	0	0
Temp. of room when set up	11.8°C.	11.8°C.	13°C.	—	13.4°C.	14.0°C.	17.2°C.	17.8°C.	17.4°C.	9.5°C.	14.1°C.
Temp. when taking samples	10°C.	11.2°C.	12.7°C.	15.2°C.	16.7°C.	16.9°C.	20.4°C.	20°C.	18.8°C.	10.2°C.	17.5°C.
Time in days.....	14	17	18	18	18	18	19	21	23	27	56
Water evap. in gms.	—	—	12.07	10.815	6.212	7.632	6.915	7.98	8.3536	—	25.18
Saturation value of N. from curve at 15°C. in { c.c. per litre	11.17	11.44	12.27	13.09	13.41	13.72	13.81	13.91	13.94	—	—
Saturation value of N. at temperature of experi- ment in c.c. per litre... }	12.27	12.28	12.79	13.037	13.02	13.26	12.59	12.47	13.047	15.31	13.29
Length of column in cms. .	317	269	269	317	317	269	269	317	317	360	317
Litres of air drawn over ...	—	—	1021	843	452	542	308	456	481	—	1734
Litres of air per 24 hrs. ...	—	—	57	47	25	30	21	22	21	—	31

obtained from observations with columns of sea and tap water, 3 feet deep and 4 cms. diameter. The columns were exposed to the air at temperatures 14°, 12°, 13·5°, 13°, and 13·5° C. for 7, 6·75, 11, 4, and 7 days respectively.

Samples of the salt solutions from the top and bottom layers of the columns, after aeration, were carefully examined by means of a Pulfrich refractometer to ascertain whether any difference in concentration of the sodium chloride existed between the two layers, but no difference could be detected.

In order to compare more clearly the experimental results obtained for the salt solution, an approximate correction for slight variations in the length of time of their exposure to the air has been made. Eighteen days was taken as the standard time, since four out of the nine tubes were exposed for that time.

Adeney and Becker's formula for calculating the rate of re-aeration was employed, viz. :—

$$w = (100 - w_1) \left(1 - e^{-f \cdot \frac{a}{v} t} \right),$$

where w = amount of gas dissolved, expressed in percentage of saturation.

w_1 = initial concentration in percentage of saturation.

f = coefficient of escape of the gas from the liquid per unit area and volume.

v = volume of liquid.

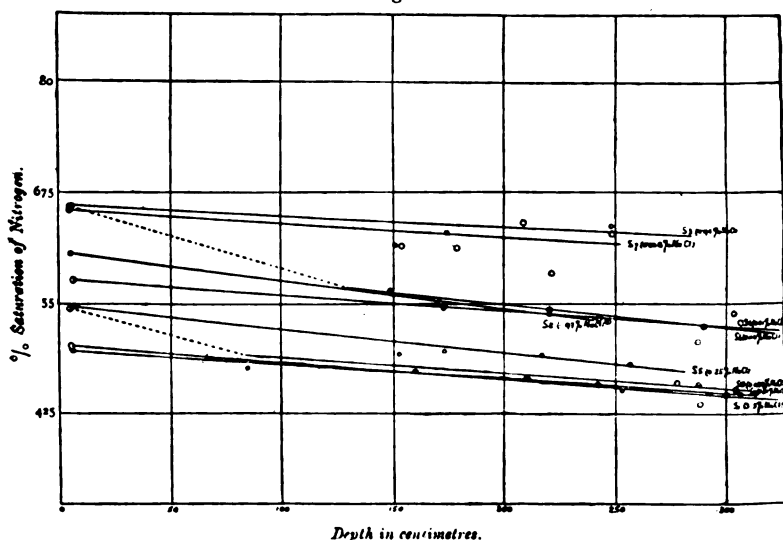
a = area of surface.

t = time of exposure.

By means of the above equation, if w be known for any time t , its value can be found for any other time t . The mean value of the concentration of the gases in solution in the liquid was taken to be w . The actual values at various depths were afterwards calculated. Curves were plotted for the columns of solutions, using observations made after eighteen days. They are given in fig. 3.

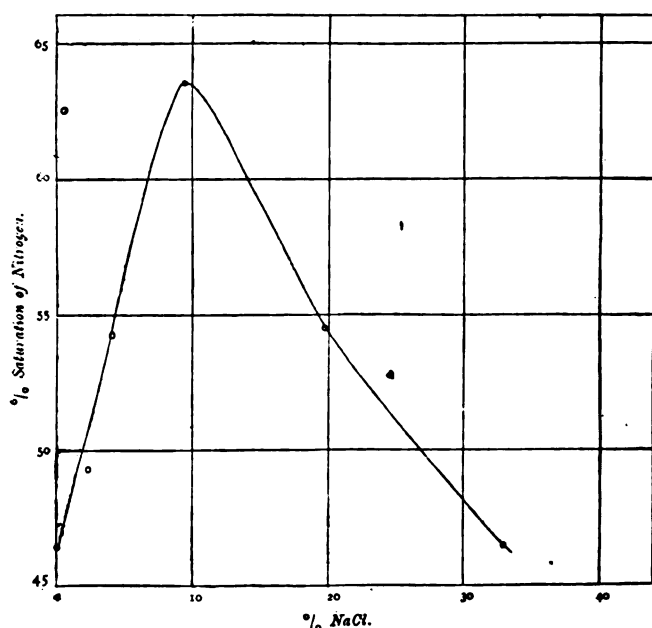
The values for the concentrations of nitrogen at a depth of 200 cms. were taken, and these values were plotted against the concentration of salt. The maximum concentration of

Fig. 3.



Concentration of Nitrogen at various depths after 18 days' exposure for different salt solutions.

Fig. 4.



Relation between NaCl concentration and downward "streaming" of dissolved Nitrogen to depths of 200 cms. through solutions of that salt.

nitrogen was found to obtain in a solution with a concentration of about 1 per cent. of sodium chloride. The curves obtained are given in fig. 4.

Conclusions.

The following conclusions may be drawn from the experimental results obtained in this investigation :—

1. The aeration of quiescent bodies of water, fresh and salt, under natural conditions is effected by a process of mixing of the exposed layer with the unexposed portions of the water to depths of at least 10 feet.

2. The process of mixing is caused by the downward "streaming" by the constantly changing layer of water exposed to the air. This downward "streaming" sets up a process of mixing certainly to depths of 10 feet, and in all probability to much greater depths.

3. The process of mixing set up by the downward "streaming" proceeds more rapidly, and more uniformly downwards, to depths of at least 10 feet, in salt water than in fresh water.

4. The rate at which the "streaming" proceeds depends largely, though not wholly, upon the rate at which the concentration and cooling of the surface layer of the water is brought about by evaporation from it.

5. The process of "streaming," and consequently of mixing, also proceeds more rapidly at temperatures at and above 10° C. than below it. It is distinctly less rapid and less uniform downwards to 10 feet deep, and probably to greater depths, at temperatures below 8° C., especially in fresh waters.

6. The rate at which the process of mixing from "streaming" proceeds also depends upon the concentration of salt in solution. The optimum concentration appears to be about 1 per cent. sodium chloride.

This last conclusion is based upon one series of experiments only, and should be confirmed by further experiments which the authors hope shortly to carry out.

Chemical Division,
Royal College of Science, Dublin.

LXXXVI. *Tables of the Bessel Function $I_n(x)$.* By HUGH E. H. WRINCH, *M.I.Mech.E., and DOROTHY WRINCH, D.Sc., Fellow of Girton College, Cambridge, and Member of the Research Staff, University College, London* *.

WHILE Tables of the Bessel Functions of both kinds, $J_n(x)$ and $Y_n(x)$, are now fairly complete, much work remains to be done in regard to the corresponding tables for the so-called "Functions of Imaginary Argument," $I_n(x)$ and $K_n(x)$, which are of considerable importance in physics.

In the present paper we give a table of the values of $I_n(x)$, where $n=0, 1, \dots, 6$, at intervals of a unit, and $x=5, 6, 7, \dots, 15$, at intervals of a unit.

The function may be defined by

$$I_\eta(x) = e^{-\eta} J_\eta(ix), \quad (\iota = \sqrt{-1}),$$

$$= \frac{x^\eta}{2^\eta \Gamma(\eta + 1)} \left\{ 1 + \frac{x^2}{2^2 1! \eta + 1} + \frac{x^4}{2^4 2! \eta + 1 \eta + 2} + \dots \right\},$$

and for large values of x , it possesses the asymptotic expansion,

$$I_\eta(x) = \frac{e^x}{\sqrt{2\pi x}} \left\{ 1 + \frac{1^2 - 4\eta^2}{1! 8x} + \frac{(1^2 - 4\eta^2)(3^2 - 4\eta^2)}{2! (8x)^2} + \dots \right\}.$$

Previous tables of this function have been almost entirely limited to the functions $I_0(x)$, $I_1(x)$ of orders unity and zero. The British Association report for 1896 gives $I_0(x)$ to nine places from $x=0$ to 5.100 at intervals of 0.001, following on a table of $I_0(x)$ of the same character in 1893. Aldis (1899) † gives $I_0(x)$ and $I_1(x)$ to twenty-one places at intervals of 0.1 from $x=0$ to $x=6$, and a few extra values.

Anding (Leipzig, 1911) published tables of the logarithms of these functions, $I_0(x)$, $I_1(x)$, from $x=0$ to 10, at intervals of 0.01. The British Association Committee in 1889 published some tables of the more general function $I_n(x)$ to twelve figures for $n=0, 1, 2, \dots, 11$, $x=0$ to 6, with intervals 0.2 in x . These were calculated from $I_0(x)$ and $I_1(x)$ by the use of the recurrence formula,

$$I_{\eta-1}(x) - I_{\eta+1}(x) = \frac{2\eta}{x} I_\eta(x).$$

For a complete bibliography of the subject, reference may be made to Watson's 'Theory of Bessel Functions,' p. 655.

* Communicated by the Authors.

† Proc. Roy. Soc. lxiv. p. 218 (1899).

Tables of the Bessel Function $I_n(x)$.TABLE I.— $I_n(x)$.

x .	$I_0(x)$.	$I_1(x)$.	$I_2(x)$.	$I_3(x)$.	$I_4(x)$.	$I_5(x)$.	$I_6(x)$.
5.0	27.2400	24.3353	17.5062	10.3307	5.10987	2.16643	.797805
6.0	67.2337	61.3426	46.7862	30.1509	16.6373	7.96810	3.36623
7.0	168.591	156.039	124.009	85.1770	51.0027	26.8654	12.5652
8.0	427.562	399.875	327.599	236.078	150.536	85.5419	43.61815
9.0	1093.59	1030.92	864.500	646.694	433.360	261.479	142.830
10.0	2815.69	2671.02	2281.52	1758.39	1226.47	777.171	449.274
11.0	7288.49	6948.85	6025.05	4757.93	3429.81	2263.59	1372.05
12.0	18949.0	18141.4	15925.5	12832.8	9508.82	6493.73	4097.54
13.0	49444.5	47502.6	42136.0	34538.3	26195.5	18417.5	12028.4
14.0	129419	124707	111603	92821.3	71823.3	51778.1	34837.1
15.0	339646	328126	295901	249217	196212	144568	99826.9

A demerit of the recurrence formula is the accumulation of the errors, which ultimately, as in all such cases, renders it unsatisfactory in that the possible error cannot be specified.

The tables we now give were calculated directly from the asymptotic expansion, and the recurrence formula was only used as a check at suitable intervals. When used in this way, it leaves nothing to be desired.

The resulting tables are in all cases correct to five significant figures. Six figures are given, and are usually correct, though the sixth figure must be regarded as approximate.

TABLE II.—Log $\Gamma(x+1)$.

x .	Log $\Gamma(x+1)$.	x .	Log $\Gamma(x+1)$.
1	·000000	15	12·1164997
2	·3010300	16	13·3206197
3	·7781513	17	14·5510686
4	1·3802113	18	15·8063411
5	2·0791813	19	17·0850947
6	2·8573326	20	18·3861247
7	3·7024306	21	19·7083440
8	4·6055206	22	21·0507667
9	5·5597631	23	22·4124945
10	6·5597631	24	23·7927057
11	7·6011558	25	25·1906457
12	8·6803370	26	26·6056190
13	9·7942804	27	28·0369828
14	10·9404084	28	29·4841408

TABLE III.

x .	$\sqrt{2\pi x}$.	e^x .	e^{-x} .	$\frac{e^x}{\sqrt{2\pi x}}$.	$\frac{e^{-x}}{\sqrt{2\pi x}}$.
1	2·50663	2·71828	·367879	1·08444	·146763
2	3·54491	7·38905	·135335	2·08441	·038177
3	4·34161	20·0855	·049787	4·62629	·011467
4	5·01326	54·5981	·018316	10·8908	·003653
5	5·60499	148·413	·006738	26·4787	·001202
6	6·13996	403·429	·002479	65·7055	·000404
7	6·63191	1096·63	·000912	165·357	·000137
8	7·08981	2980·96	·000335	420·456	·000047
9	7·51989	8103·08	·000123	1077·55	·000016
10	7·92665	22026·5	·000045	2778·78	·000006
11	8·31355	59874·1	·000017	7202·00	·000002
12	8·68321	162755	·000006	18743·6	·000001
13	9·03778	442414	·000002	48951·6	·000000
14	9·37894	120260	·000001	128224	
15	9·70813	326902	·000000	336730	
16	10·0265	888611		886261	
17	10·3351	241549		233718	
18	10·6347	656600		617411	
19	10·9261	178482		163354	
20	11·2100	485165		432797	

Certain subsidiary tables are also given, whose calculation was a necessary preliminary. They are of types which are frequently needed. Table II., for example, gives the values of $\log \Gamma(n+1)$ or $\log (n!)$ from $n=1$ to 28, to seven significant figures. They are calculated from the seven figure logarithms of Chambers, and therefore should certainly be correct to five significant figures.

Table III. is of the same type as a table given in Jahnke and Emde's 'Funktionentafeln' (Leipzig and Berlin, 1909). It gives the values of e^x , e^{-x} , $e^x/\sqrt{2\pi x}$, $e^{-x}/\sqrt{2\pi x}$ from $x=1, 2, 3, \dots 20$.

LXXXVII. *The Calculation of the Electric Moment of the Molecule of a Substance.* By CHARLES P. SMYTH, *Ph.D.*,
Department of Chemistry, Princeton University *.

THE system of electrons and positive nuclei constituting a molecule may be regarded as an electric doublet. This doublet may be very small, or it may be so large that its charges tend toward separation by ionization. According to the magnitude of this doublet as exhibited in the properties of a substance, the substance is qualitatively classified as polar or non-polar †. Inasmuch as the doublet in a molecule may be neither very small nor very large, the classification is not a sharp one. The actual measure of the magnitude of a doublet is its electric moment, a quantity which has been determined for the molecules of very few substances. The electric moment of a molecule may be defined as the product of the distance between the "centres of gravity" of the positive and negative constituents of the molecule by the total charge of either sign. A knowledge of its value is of obvious interest in testing theories of molecular structure and also in leading to a precise explanation of those properties of a substance which lead to its classification as polar or non-polar.

The present paper, which has been developed in connexion with an experimental investigation of the subject, describes a method by which the moments of the permanent electric doublets in the molecules of many substances may be calculated from data already available.

* Communicated by Prof. K. T. Compton.

† G. N. Lewis, *Jour. Amer. Chem. Soc.* xxxviii, p. 762 (1916); xxxv, p. 1448 (1913). W. C. Bray and G. E. K. Branch, *Jour. Amer. Chem. Soc.* xxxv, p. 1440 (1913).

EQUATIONS OF DEBYE AND THOMSON.

It has been found that the existence of a permanent electric doublet in the molecule of a substance contributes to the value of the dielectric constant of the substance, when the molecule is free to move, owing to the tendency of the molecule to orient itself in the electric field, thus adding to the electric polarization of the medium. When the molecule is rigidly constrained and unable thus to orient itself, as in solids, this contribution disappears. The relation was first formulated by Debye * for gases at constant volume :

$$\epsilon = \epsilon_0 + \frac{a}{T}, \quad (1)$$

in which ϵ is the dielectric constant, T the absolute temperature, and ϵ_0 and a are constants, the term $\frac{a}{T}$ containing the contribution of the moments of the permanent doublets. For liquids, the expression developed was

$$\frac{\epsilon - 1}{\epsilon + 2} = b + \frac{a}{T} (2)$$

b and a are assumed to be constant for a given liquid, a being connected with the electric moment μ by the expression

$\mu = \frac{3}{\sqrt{4\pi}} \sqrt{\frac{ka}{N}}$, in which k is the Boltzmann-Planck constant and N the number of molecules per cm.³ In the development of this equation, the change in volume accompanying change in temperature of the liquid is treated as negligible, and it is assumed that the molecule has a permanent electric moment upon which an induced moment may be superimposed by the application of an external electric field. The equation takes account of the orienting influence of the molecules upon one another because of their electric fields only by including the average field due to doublets at a considerable distance from the region under consideration.

Thomson † has derived an equation for gases similar to that given by Debye. It is assumed that the density of the gas is constant and equal to the density when the temperature is 0° C. and the pressure 760 mm. The equation then is

$$\epsilon = a + \frac{.88\mu^2 \times 10^{36}}{T} (1a)$$

where ϵ , μ , and T have their usual significance, and a is a

* P. Debye, *Phys. Zeit.* xiii. p. 97 (1912).

† J. J. Thomson, *Phil. Mag.* (6th series), xxvii. p. 757 (1914).

constant assumed to be independent of temperature. The numerical factor comes as the result of replacing all universal constants by their numerical values. If ϵ_1 and ϵ_2 are the values of the dielectric constant at the temperatures T_1 and T_2 , substitution in the above equation and subtraction gives the equation

$$\epsilon_1 - \epsilon_2 = .88\mu^2 \times 10^{36} \left(\frac{1}{T_1} - \frac{1}{T_2} \right), \quad \dots \quad (3)$$

from which μ may be calculated directly.

EQUATION OF GANS.

A more general equation has been developed by Gans* and discussed and tested by Gans and Isnardi†. This equation is developed on the assumption that the molecule has a permanent electric moment upon which an induced moment may be superimposed, and it takes account of the mutual influence of the molecules on the assumption that the forces acting between them are isotropic. The equation may be written :

$$\frac{\epsilon - 1}{\epsilon + 2} \frac{1}{D} = \frac{4\pi N_0}{3M} g + \frac{16\sqrt{\pi}\mu^2 N_0^2}{9RMT} \Phi(\tau), \quad \dots \quad (4)$$

in which D is the density ; N_0 is the number of molecules in one gram-molecule ; M is the molecular weight ; g is the constant of "quasi-elastic linking," that is, the moment induced in the molecule by unit exciting force ; R is the universal gas constant ; and

$$\begin{aligned} \tau &= \frac{kT}{\mu E_0} = \frac{3R}{4N_0^2 \mu^2} \sqrt{\frac{s^3 M N_0}{\pi}} \cdot \frac{T \sqrt{1 - \gamma D}}{\sqrt{D}} \\ &= \frac{T \sqrt{1 - \gamma D}}{B \sqrt{D}}, \quad \dots \quad (5) \end{aligned}$$

where $\gamma = \frac{8\pi N_0 g^2}{3s^3 M}, \quad \dots \quad (6)$

$$B = \frac{3R}{4N_0^2 \mu^2} \sqrt{\frac{s^3 M N_0}{\pi}}, \quad \dots \quad (7)$$

s = the smallest distance between the centres of two molecules,

* R. Gans, *Ann. d. Phys.* (4) lxiv. p. 481 (1921).

† H. Isnardi and R. Gans, *Phys. Zeits.* xxii. p. 230 (1921). H. Isnardi, *Zeits. f. Phys.* ix. p. 152 (1922); see also P. Lertes, *Zeits. f. Phys.* vi. p. 257 (1921).

that is, the molecular diameter; $k = \frac{R}{N_0}$, the Boltzmann-Planck constant, and E = the most probable molecular field. If we substitute

$$\frac{16 \sqrt{\pi} \mu^2 N_0^2}{9RM} = A \quad \dots \quad (8)$$

and

$$\frac{4\pi N_0}{3M} g = C, \quad \dots \quad (9)$$

the equation becomes

$$\frac{\epsilon - 1}{\epsilon + 2} \frac{1}{D} = C + \frac{A}{T} \Phi \left(\frac{T \sqrt{1 - \gamma D}}{B \sqrt{D}} \right) \quad \dots \quad (10)$$

also

$$\gamma = \frac{8}{3\pi} \left(\frac{BC}{A} \right)^2 \quad \dots \quad (11)$$

C may be calculated from the dispersion curve for the visible region of the spectrum by means of the following equation :

$$\frac{m^2 - 1}{m^2 + 2} \frac{1}{D} = \frac{C}{1 - \frac{\lambda_0^2}{\lambda^2}}, \quad \dots \quad (12)$$

in which m is the index of refraction for light of wave-length λ , and λ_0 is the wave-length corresponding to a characteristic vibration frequency in the ultra-violet region.

$\Phi(\tau)$ is a function originally introduced by Gans* in his theory of paramagnetism as $\Phi(\tau) = \tau \psi(\tau)$. For small values of τ , $\psi(\tau)$ may be represented by the series

$$\psi = 1 - \frac{\tau \sqrt{\pi}}{2} + \frac{1}{60} (\pi \tau)^4 - \frac{1}{126} (\pi \tau)^6 + \frac{1}{240} (\pi \tau)^8 - \dots, \quad (13)$$

while for large values of τ ,

$$\psi = \frac{\sqrt{\pi}}{4\tau} \left(1 - \frac{1}{6\tau^2} + \frac{1}{18\tau^4} - \frac{1}{40\tau^6} + \dots \right) \quad \dots \quad (14)$$

For very large values of τ , that is, for high temperatures and low densities, as in the case of uncompressed gases, $\tau \psi(\tau)$ assumes the constant value $\frac{\sqrt{\pi}}{4}$, so that, for this special case,

$$\frac{\epsilon - 1}{\epsilon + 2} \frac{1}{D} = C + \frac{A}{T} \frac{\sqrt{\pi}}{4}, \quad \dots \quad (10a)$$

* R. Gans, *Ann. d. Phys.* (4) 1. p. 163 (1916).

which is similar in form to equation (2), except for the presence of the factor $\frac{1}{D}$ on the left, which Debye, as an approximation, treated as constant for liquids.

In the original equation (10) the constants A and B, since γ can be expressed in terms of A, B, and C, are the only quantities which cannot be experimentally determined or calculated directly. By obtaining C from optical data, determining ϵ and D at several different temperatures, and successively substituting these values in the equation, A and B may be calculated by the method of successive approximations. μ is then obtained by means of equation (8).

Isnardi* has tested the validity of the equation for ether and chloroform over a wide range of temperature, and has further tested it on a number of other substances by calculating the dielectric constant in the vapour state from data for the liquid, obtaining good agreement between the calculated and the observed values. Lertes† has applied it successfully to chloroform and toluene.

The accuracy with which the equation represents the behaviour of these liquids is strong evidence of its validity. It is thus apparent that knowledge of the refractive indices of a substance for light of different wave-lengths (two or more) and of the densities and dielectric constants at a number of different temperatures makes possible the calculation of the electric moment of the molecule of the substance.

NEW METHOD OF CALCULATION.

In the present work, a somewhat different method has been developed for the calculation of the moment. In equation (4), $\tau\psi(\tau)$ may be substituted for $\Phi(\tau)$, and τ replaced by the expression given for it in (5). We then get

$$\frac{\epsilon - 1}{\epsilon + 2} \frac{1}{D} = \frac{4\pi N_0}{3M} g + \frac{4}{3} \sqrt{\frac{s^3 N_0}{M}} \sqrt{\frac{1 - \gamma D}{D}} \psi(\tau).$$

Substitution for γ of its value obtained from equation (6) gives

$$\frac{\epsilon - 1}{\epsilon + 2} \frac{1}{D} = \frac{4\pi N_0}{3M} g + \frac{4}{3} \sqrt{\frac{s^3 N_0}{MD} - \frac{8\pi N_0^2 g^2}{3M^2}} \psi(\tau).$$

Substitution for g of its value obtained from equation (9) gives

$$\frac{\epsilon - 1}{\epsilon + 2} \frac{1}{D} = C + \frac{4}{3} \sqrt{\frac{s^3 N_0}{MD} - \frac{3C^2}{2\pi}} \psi(\tau). \quad \dots \quad (15)$$

* *Loc. cit.*

† *Loc. cit.*

For a given substance, ϵ , D , and $\psi(\tau)$ are the only variables contained in equation (15). The experimental determination of ϵ and D , accordingly, makes possible the calculation of the corresponding value of $\psi(\tau)$. From $\psi(\tau)$, the value of τ may be obtained by equations (13) and (14), and, with τ known, μ may be calculated.

In order to find τ from $\psi(\tau)$ we may use the solutions of equations (13) and (14), given by Gans*, as shown in Table I.

TABLE I.
Relation between τ and $\psi(\tau)$.

τ .	$\psi(\tau)$.	τ .	$\psi(\tau)$.
0.0	1.0000	3.0	0.1451
0.1	0.9115	3.3333	0.1310
0.2	0.8249	4.0	0.1097
0.25	0.7825	5.0	0.08806
0.5	0.6013	8.0	0.05526
1.0	0.3867	10	0.04425
1.25	0.3231	15	0.02953
1.4286	0.2883	20	0.02215
1.6667	0.2516	25	0.01773
2.0	0.2131	30	0.01477
2.5	0.1727	∞	0.00000

By plotting graphically on a large scale the values of $\psi(\tau)$ against those of τ , a curve is obtained from which the value of τ corresponding to any value of $\psi(\tau)$ may be accurately read off. Equation (15) thus provides a means of calculating τ .

To find the value of μ we substitute the value of γ from equation (6) into the third member of equation (5), giving

$$\tau = \frac{3RT}{4\mu^2 N_0^2} \sqrt{\frac{s^3 M}{\pi N_0 D} - \frac{8}{3} g^2}.$$

We next substitute the value of g from equation (9) and solve for μ , obtaining

$$\mu = \sqrt{\frac{3RT}{4N_0\tau}} \sqrt{\frac{s^3 M}{\pi N_0 D} - \frac{3M^2 C^2}{2\pi^2 N_0^2}}. \quad (16)$$

μ may thus be calculated from the value of τ corresponding to that of $\psi(\tau)$ obtained from equation (15). Equations (12), (15), and (16) render possible the calculation of μ , the

* R. Gans, *Ann. d. Phys.* lxiv. p. 498 (1921).

electric moment of the molecule of a substance, in the liquid or gaseous state, from the indices of refraction at two different wave-lengths, the density of the substance under the conditions under which these indices are measured, one value of the dielectric constant together with the temperature at which it is measured, the density at this temperature, the molecular diameter, the molecular weight, and certain universal constants. In order to calculate the moment through the constant A , as obtained by Isnardi and Gans (*cf.* equations (8) and (10)), it is necessary to have all of these data with the exception of the molecular diameter and the addition of the values of the dielectric constant and the corresponding density at a number of different temperatures. The necessary values of the refractive indices and the accompanying densities are available for a large proportion of the substances which may come up for consideration, but the dielectric constants of most substances have been measured within so small a temperature range as to make the method of Isnardi and Gans impracticable until our experimental knowledge of the temperature dependence of dielectric constants is considerably extended.

The molecular diameter, which is the only quantity required in this new method of calculation that is not required in the method used by Isnardi and Gans, has been defined as the smallest distance by which the centres of any two molecules can be separated. This is the molecular diameter as ordinarily used in the kinetic theory of gases, and may, therefore, be calculated from viscosity data or from the value of the constant b in van der Waals' equation. The values thus obtained are not always reliable*, and may, in some cases, introduce errors into the values of the moments calculated from them. Fortunately, however, a large error in the value of the diameter produces, as a rule, a relatively small error in the calculated value of the moment because of the form of the equations used.

Equations (15) and (16) contain two terms under the square root sign, the second of which, $\frac{3C^2}{2\pi}$ and $\frac{3M^2C^2}{2\pi^2N_0^2}$, are constant for any given substance and small in comparison with the first. In both equations, the first term under the square root sign is larger, the lower the density. For gases, therefore, the second term is quite negligible in comparison with the first and, indeed, for liquids, the error introduced by the omission of the second term from both equations is small.

* J. H. Jeans, 'Dynamical Theory of Gases,' chapter xiv.

RESULTS OBTAINED FROM THE DIFFERENT EQUATIONS.

The application of the different equations to various substances is illustrated by the results given in the following tables, in which the first column gives the temperature on the centigrade scale at which the value of the dielectric constant given in the second column is observed, while the third column gives the corresponding density, and the fourth column the calculated value of the moment multiplied by 10^{18} . The fifth column shows the method of calculation used, and includes any necessary explanation. The method described as "Eq. (15) and (16) simplified" is that in which the terms $\frac{3C^2}{2\pi}$ and $\frac{3M^2C^2}{2\pi^2N_0^2}$ are neglected. The similarity of equation (10a) to equation (2) has already been noted. When equation (10a) is used in the calculation of μ , the values of ϵ and D corresponding to the upper and lower limits of the temperature interval shown in the tables are substituted in the equation, C is eliminated between the two resulting simultaneous equations, and the constant A is thus obtained. μ is then calculated from A by means of equation (8). The calculation is similar to that involved in the use of equation (3), which Thomson proposes for gases, except that a variable density is introduced.

The values used for the universal constants are $N_0 = 6.07 \times 10^{23}$ and $R = 8.315 \times 10^7$. The molecular weight is reckoned for each substance from the atomic weights of its constituent elements. The values of C and s obtained for a substance are shown in the tables above the other data for that substance. When a different value of s is used in order to determine the effect of variation in s upon the value of μ , it is given in the fifth column.

Table II. shows that, except in the neighbourhood of the freezing-point of the liquid, equations (15) and (16) give a value for μ in excellent agreement with that obtained by Isnardi and Gans, $\mu = 1.435 \times 10^{-18}$. The use of the value 4.5×10^{-8} instead of 3.39×10^{-8} for the diameter makes an appreciable difference in the value of μ , but this difference is only slightly greater than that between the value 1.26×10^{-18} obtained by Isnardi for the moment of the chloroform molecule and the value 1.358×10^{-18} obtained by Lertes for the same quantity, chloroform being the only substance for which the moment has been obtained by the method of Isnardi and Gans by two different observers. The omission

TABLE II.

Ethyl Ether ($C = .2961$; $s = 3.39 \times 10^{-8}$ cm.).

Temp. °C.	ϵ .	D.	$\mu \times 10^{18}$.	Method.
18	4.36	0.7150	1.308	Eq. (15) and (16) ($s = 4.5 \times 10^{-8}$ cm.).
"	"	"	1.446	Eq. (15) and (16)
"	"	"	1.420	Eq. (15) and (16) simplified.
-120	3.16	0.8612	0.603	Eq. (15) and (16) simplified.
-100	8.143	0.8410	1.373	" " " " "
-80	7.049	0.8205	1.373	" " " " "
-54	6.33	0.7930	1.409	" " " " "
0	4.683	0.7359	1.410	" " " " "
18	4.36	0.7150	1.420	" " " " "
160	2.41	0.4927	1.420	" " " " "
100	1.00516	0.00242	1.513	Gas. Eq. (15) and (16) simplified.
Temp. Interval (° C.).				
-54 to 0			0.932	Eq. (10 a).
0 to 18			0.383	" "
40 to 100			1.000	" "
140 to 160			1.133	" "

The data on the liquid are taken from the paper of Isnardi and Gaus (*Phys. Zeits.* xxii. p. 230 (1921)), and differ only slightly from those in the later paper of Isnardi (*Zeits. f. Phys.* ix. p. 152 (1922)). The value of ϵ for the gas is that given by K. Bädcker (*Zeits. Phys. Chem.* xxxvi. p. 304 (1901)), and the density is obtained approximately on the assumption that the vapour behaves as an ideal gas. The value $s = 3.39 \times 10^{-8}$ cm. is that calculated by Isnardi and Gaus, and is used here for the sake of comparison. The value $s = 4.5 \times 10^{-8}$ cm. is obtained by application of the kinetic theory of gases to data contained in Landolt-Börnstein, 4th edition.

of the terms $\frac{3C^2}{2\pi}$ and $\frac{3M^2C^2}{2\pi^2N_0^2}$ has only a very small effect upon the value of μ , which justifies the use here of equations (15) and (16) in the simplified form. The results obtained by means of equation (10 a) are extremely variable, and differ widely from those given by the other methods. The values of μ calculated for ether at widely different temperatures show close agreement with the exception of the value at -120° , which is just below the generally accepted value for the freezing-point of the liquid. The value for the gas at 100° is calculated from an old value of ϵ and a calculated

value of D , and shows agreement which is surprisingly good under the circumstances.

TABLE III.

Hydrogen Sulphide ($C=220$).

Temp. °C.	ϵ .	D .	$\mu \times 10^{18}$.	Method.
10	5.93	0.844	1.008	Eq. (15) and (16) simplified. ($s=3.2 \times 10^{-8}$ cm.)
50	4.92	0.776	1.045	" " " " "
90	3.76	0.707	1.023	" " " " "
10	5.93	0.844	0.920	Eq. (15) and (16) ($s=5.0 \times 10^{-8}$ cm.)
50	4.92	0.776	0.973	" " " " "
90	3.76	0.707	0.974	" " " " "
Temp. Interval (°C.).				
10 to 50		0.282	Eq. (10 a).	
50 to 90		2.921	" "	
10 to 90		2.046	" "	

$C=220$ is the average of two widely differing values calculated for the gas from data in Landolt-Börnstein, 4th edition. A large error in C has only a small effect upon the value of μ . The values of ϵ are obtained from P. Eversheim (*Ann. d. Phys.* xiii. p. 507 (1904)). D is calculated from the empirical equation, $D=1.328-0.00171T$. $s=3.2 \times 10^{-8}$ is calculated from the value of b given by Cardoso (*J. Chim. Phys.* x. p. 470 (1912)), and agrees well with the value 3.16×10^{-8} calculated from the mean collision area of the gas molecule given by A. O. Rankine and C. J. Smith (*Phil. Mag.* xlii. p. 615 (1921)). The calculations from the value $s=5.0 \times 10^{-8}$ are included to show the relatively small effect of a large error in the diameter upon the value of the electric moment.

No results are given in Table III. to show the effect of omitting the terms $\frac{3C^2}{2\pi}$ and $\frac{3M^2C^2}{2\pi^2N_0^2}$ from equations (15) and (16), although calculation shows the effect to be negligible. The values of μ for hydrogen sulphide agree well at the three different temperatures, which are remote from the freezing-point of the liquid. An increase of 56 per cent. in the value of s causes a decrease of only 7 per cent. in the value of the moment. The results calculated by means of equation (10 a) differ so widely as to be quite meaningless.

TABLE IV.

(Chlorobenzene ($C = \cdot 2660$; $s = 4\cdot 82 \times 10^{-8}$ cm.).

Temp. ° C.	ϵ .	D.	$\mu \times 10^{18}$.	Method.
-20	6.93	1.149	1.207	Eq. (15) and (16) simplified.
"	"	"	1.259	Eq. (15) and (16).
0	6.42	1.128	1.289	" " " "
20	5.94	1.106	1.427	" " " "
100	4.70	1.019	1.418	" " " "

Bromobenzene ($C = \cdot 2079$; $s = 4\cdot 92 \times 10^{-8}$ cm.).

Temp. ° C.	ϵ .	D.	$\mu \times 10^{18}$.	Method.
-20	6.40	1.548	1.258	Eq. (15) and (16).
0	5.90	1.522	1.267	" " " "
20	5.53	1.495	1.286	" " " "
100	4.56	1.386	1.391	" " " "

For both substances, the values of the refractive indices and densities for calculation of C are obtained from Landolt-Börnstein, 4th edition. The values of ϵ and D are those given by Lertes (*loc. cit.*). s is calculated from the values of b obtained from the data of S. Young (Sci. Proc. Roy. Dublin Soc. n. s. xii. p. 374 (1909-10)).

The data on chlorobenzene and bromobenzene are tabulated together because of the similarity of these two substances.

For chlorobenzene, the effect of omitting the terms $\frac{3C^2}{2\pi}$ and $\frac{3M^2C^2}{2\pi^2N_0^2}$ is greater than in the case of ether or hydrogen sulphide, but is still small. The apparent value of μ for chlorobenzene, which freezes at -45° , increases with rise of temperature from -20° to $+20^\circ$, where it seems to become constant, while, for bromobenzene, which freezes at $-30\cdot 5^\circ$, it is still rising at 20° , although it may be constant before 100° is reached. The lack of further data leaves this uncertain. The variation of the calculated values of μ with temperature is, however, not great, and seems to disappear altogether at temperatures well removed from the freezing-point of the liquid.

TABLE V.

Methyl Alcohol ($C = \cdot 250$; $s = 3 \cdot 72 \times 10^{-8}$ cm.).

Temp. ° C.	ϵ .	D.	$\mu \times 10^{18}$.	Method.
-100	60.0	.9091	1.019	Eq. (15) and (16).
-70	51.5	.8787	1.142	" " " "
-40	44.0	.8503	1.234	" " " "
-10	37.5	.8217	1.336	" " " "
0	35.0	.8100	1.352	" " " "
20	31.2	.7915	1.434	" " " "
78.1	1.00745	.001112	1.931	Eq. (15) and (16) (Gas).
93.3	1.00655	.001066	1.855	" " " " "
107.8	1.00589	.001025	1.799	" " " " "
125.4	1.00531	.000980	1.777	" " " " "
144.0	1.00476	.000936	1.756	" " " " "
168.2	1.00449	.000885	1.795	" " " " "
178.1	1.00431	.000866	1.809	" " " " "

For the liquid, the values of ϵ are obtained from the measurements of R. Abegg and W. Seitz (*Zeits. Phys. Chem.* xxix. p. 242 (1899)), and the values of D from the work of W. Seitz, H. Alterthum, and G. Lechner (*Ann. d. Phys.* (4) xlix. p. 91 (1916), quoted by Isnardi (*loc. cit.*)) as well as from Landolt-Börnstein, 4th edition. For the gas, the values of ϵ are those given by M. Jona (*Phys. Zeits.* xx. p. 14 (1919)), and the densities are calculated on the assumption that the vapour behaves as an ideal gas, a procedure which is justifiable only because of the considerable errors probably occurring in the measurements of the dielectric constant.

The data on methyl alcohol are included because they cover the substance in both the liquid and the gaseous state. Unfortunately, a considerable gap in the data occurs between the liquid at 20° and the gas at 78°.1 . The calculated value of μ for the liquid shows no approach to the constancy attained in the case of the other substances studied, but increases from the freezing-point almost as a linear function of the temperature. The value for the gas at 78°.1 , which is only 12° above the boiling-point, is considerably higher than that for the liquid at 20° , but a small decrease occurs with rise of temperature. The very small increase which follows this decrease appears to be accidental, and may be attributed to small errors in the data. Indeed, one might be tempted to attribute all the variation in the value of μ for the gas to errors in the data, were it not that Jona's results point to a similar behaviour on the part of sulphur dioxide and water vapour in the neighbourhood of their boiling-points, and to a

smaller but similar effect in the case of ammonia, which was investigated at temperatures farther above the boiling-point. Jona explains the high value obtained for μ near the boiling-point as being due to molecular association, which alters the molecular concentration in this region, but becomes negligible at higher temperatures.

Of the liquids which have been discussed, only methyl alcohol is known to be strongly associated, and it is the only one which shows a steady increase in the apparent value of μ over the entire range of temperature in which it is investigated as a liquid. The apparent values of μ for the non-associated liquids generally show some increase as the temperature rises in the neighbourhood of the freezing-point, but soon attain constancy. The application of equations (15) and (16) to a crystalline or amorphous solid, in which the molecules are not free to move about, would lead to a calculated value of approximately zero for μ . In the immediate neighbourhood of the freezing-point of a liquid, the molecules, presumably, lack complete freedom of motion, because of the formation of aggregates, so that the values calculated for μ in this region of temperature might be expected to be low. As the temperature rises and this lack of freedom disappears, the calculated value of μ should approach the constant, true value. The effect of molecular association may be supposed to be similar to that produced by the molecular aggregation in the neighbourhood of the freezing-point—that is, lack of complete freedom of motion on the part of the molecules leads to calculated values of μ which are too low. As the degree of association decreases with rise of temperature, the calculated values of μ increase, reaching no constant value as long as association persists. In the gaseous state, where the intermolecular distances are large, the influence of association may be of quite another character, the predominating effect being, perhaps, that of change in concentration, as assumed by Jona, so that the alteration of μ with temperature in the gaseous condition may be altogether different from that in the liquid.

In equation (15) the values of s , M , and D are so increased by association that the term under the radical sign is somewhat decreased, and $\psi(\tau)$ may be considerably decreased because of the increase caused in the value of τ , as is evident from equation (16) and Table I. In the application of the equation to an associated liquid, no account is taken of the effect of association in increasing the values of s and M , which, because of our ignorance of the actual effect, are

treated as constants. The result is that the values of μ obtained in such calculations are smaller than the true ones, and approach the latter only as the true values of ϵ and M approach the values used for them in the calculations. This would seem to explain the behaviour of the liquids when agglomeration in the neighbourhood of the freezing-point or association occurs.

The method of using the Gans equation suggested in this paper has another distinct advantage over that used by Isnardi and Gans in addition to its greater range of applicability. When applied to associated liquids the Isnardi and Gans method may lead to serious errors, which are minimized and detected by the present method.

This is made evident by a consideration of the two ways in which temperature affects the dielectric constant. Decreasing the temperature increases the dielectric constant by permitting increased alignment of the permanent doublets, and may also decrease the dielectric constant by increasing the degree of association—which latter effect is not taken account of in the equations. In strongly associated liquids this latter effect may nearly balance the former, so that the dielectric constant would show little variation with temperature.

In such cases the method of Isnardi and Gans would lead to the false conclusion that the molecular doublets possess very small moments. The present method would yield a value of the right order of magnitude, though too small, and would indicate the nature of the error by the failure of the calculated moment to take a constant value with increasing temperature.

Examples of this type of error may be cited. Isnardi finds that with carbon tetrachloride, carbon bisulphide, benzene and m-xylol, substances with very small electric

moments, $\frac{\epsilon - 1}{\epsilon + 2} D$ actually decreases with decreasing temperature, which would lead to an imaginary value for the moment if it were calculated from the value of ϵ at different temperatures. Again, with both methyl and ethyl alcohol $\frac{\epsilon - 1}{\epsilon + 2} D$ decreases with decreasing temperature, a circumstance which led Isnardi to class these substances with carbon tetrachloride, carbon bisulphide, benzene, and m-xylol as substances with practically no molecular electric moments. The present method, however, shows methyl and ethyl alcohol to have large electric moments, as is to be expected

from their strongly polar properties, and gives evidence of the effect of association which vitiates the older method. In the absence of complicating circumstances, such as association, the two methods should, of course, agree.

From these results, which have been selected as typical from among a considerable number of calculations, it may be concluded that equation (10 a), which resembles the Debye equation except for the presence of the factor $\frac{1}{D}$, cannot be applied to liquids, although it should represent the behaviour of gases at high temperatures and low pressures. Equations (15) and (16) may be used to calculate the moments of the molecules of substances in both the liquid and the gaseous states, provided that there is no association or agglomeration of the molecules. This complication may be avoided in the case of non-associated liquids by working at temperatures considerably removed from the freezing-point. In the case of highly associated liquids, the true value of the moment of the single molecule is not given by equations (15) and (16), so that the substance must be studied in the gaseous condition. The fact that this method of calculation gives the value of the moment at a definite temperature, instead of the average value over a wide range, makes possible the detection of a variation with temperature, and hence of a change in the degree of molecular aggregation with temperature. It is thus possible to gain more accurate knowledge of the true values of the moments of many substances, and it is hoped that the application of these equations to associated liquids may throw some light upon the phenomena of association.

Some of the experimental aspects of this problem, which was originally suggested by Professor K. T. Compton, are being investigated in the Palmer Physical Laboratory with special apparatus made available through a grant from the Joseph Henry Fund of the National Academy of Sciences.

The writer wishes to acknowledge his deep indebtedness to Professor Compton for much helpful advice and criticism.

SUMMARY.

The simple form of equation proposed by Debye to represent the temperature variation of the dielectric constant of a substance cannot be used to calculate the electric moment from data upon the substance in the liquid condition.

A method is described whereby the electric moment of the molecule of a substance in the liquid or gaseous state may be

calculated from the indices of refraction at two different wave-lengths, the density of the substance under the conditions under which these indices are measured, the dielectric constant at one temperature, the density at this temperature, the molecular diameter, and certain universal constants.

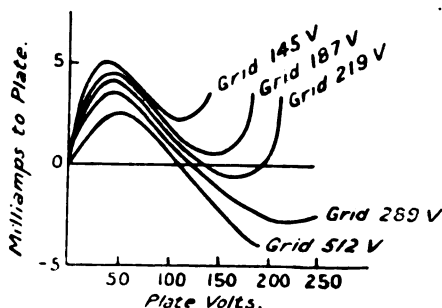
For normal liquids this method gives results in good agreement with those obtained by the method of Isnardi and Gans. For associated liquids, it leads to results which are low but which give an idea of the magnitude of the moment, while the method of Isnardi and Gans may lead to serious errors for such liquids.

Princeton, New Jersey, U.S.A.

LXXXVIII. *The Emission of Secondary Electrons from Nickel.* By E. W. B. GILL, M.A., B.Sc., Fellow of Merton College, Oxford*.

1. **S**OME experiments recently made by Hull† on secondary emission, using a three-electrode valve at the lowest possible pressure, gave the results shown by the curves in fig. 1. In these experiments a stream of

Fig. 1.



electrons leave the hot filament whose potential may be taken as zero, and are attracted to the grid whose potential is $+V_G$; a proportion pass through and reach the plate whose potential is $+V_P$. The curves show the currents in the plate circuit for various values of V_P ; V_G being kept constant for each curve. So long as V_G is greater than V_P , any secondary electrons leaving the plate will be collected on

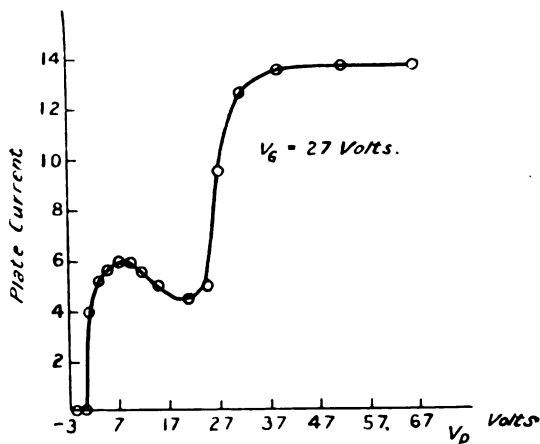
* Communicated by Prof. J. S. Townsend, F.R.S.

† Hull, Proc. Inst. Radio Engineers, Feb. 1918.

the grid, and the plate current correspondingly reduced. The velocity of impact on the plate of the primary electrons depends only on V_p , the total potential through which they fall after leaving the filament, and the increase of secondary emission with velocity of impact is shown by the downward slopes of the curves after V_p reaches the value of from 20 to 30 volts. Hull was chiefly interested in the application of these results to wireless telegraphy, the falling characteristic indicating instability and rendering it possible to use such an arrangement for the production of continuous oscillations or for the magnification of small potentials and currents; and I cannot find that he has given anywhere a detailed analysis of the curves.

Horton and Miss Davies * have also obtained a similar curve and put forward some explanations of it, but these explanations are not in agreement with the results of a series of experiments I have recently made.

Fig. 2.



They used plane and not cylindrical electrodes, the plate being of platinum. A slit was inserted between the filament and grid, and a magnetic force was applied perpendicular to the electrodes to keep the stream of electrons moving as far as possible in the same direction.

Their results are given by the curve (fig. 2) which, following the usual practice with valves, is plotted with the plate current through the valve indicated by ordinates

* Horton & Miss Davies, Proc. Roy. Soc. A. *xcvii.* p. 23 (1920).
Phil. Mag. Ser. 6. Vol. 45. No. 269. May 1923. 3 K

measured upwards. The abscissæ represent the plate potentials V_P , the grid being maintained constant at 27 volts.

As V_P increases, the various portions of the curve were explained as follows:—

- (A) The first rise is due to the electrons from the filament getting to the plate.
- (B) The nearly flat portion at the first maximum is due to the reflexion of the impacting electrons.
- (C) The drop is due to secondary emission of electrons whose excitation requires a minimum applied potential of from 10 to 11 volts and becomes of increasing importance as V_P increases.
- (D) After the minimum at about $V_P=20$ volts the number of secondary electrons leaving the plate decreases.
- (E) The final constant current which is attained at about 36 volts—that is, when the plate is 9 volts positive to the grid—indicates that the maximum velocity of the electrons leaving the plate is equivalent to that acquired by a fall through a potential difference of 9 volts.

These explanations will be considered later, but it may be remarked with regard to (B) that it does not appear that such experiments can discriminate between electrons which are reflected and secondary electrons emitted from the plate due to the impact of the primary stream. The proof that the whole phenomenon is not due to reflexion alone is that, as will be seen later, the number of electrons emitted from the plate can exceed the number that impinge on it, and the general smoothness of the curves renders it unlikely that at any point there is an abrupt transition from reflexion to emission; and as it is impossible by means of such experiments to distinguish emission from reflexion, all electrons receding from the plate will be referred to as secondary emission in this paper.

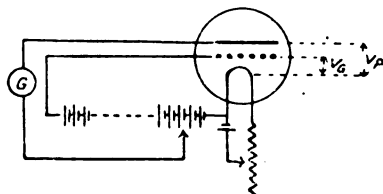
Some very recent work by Davisson and Kunsman* indicates that secondary emission occurs from nickel for values of V_P down to almost zero, and that these electrons are practically all emitted with low velocities, the number emitted with a high velocity being negligible. Their paper, however, is all contained in a short abstract of a few lines, and it is impossible to obtain details of their experiments.

* Davisson & Kunsman, *Phys. Rev.* 20, 1, p. 110.

The following experiments on secondary emission were made in order to obtain a satisfactory explanation of the anode currents under these conditions, and are interesting as emphasizing certain effects of grids which are now very largely used in determining critical potentials, and whose action in this connexion is not always sufficiently considered.

2. The experimental arrangements are shown by the diagram (fig. 3). The three-electrode valve used was a Marconi M.T. 5, described in detail in a recent paper (Phil. Mag., July 1922, p. 165), the vacuum being very low. The grid, and plate which was of nickel, were both cylindrical, the filament being along the axis. The grid was of square mesh of side about 1.5 mm. made of thin wire, the diameter of the grid and plate cylinders being 1 and 2.5 cms. respectively. The filament was heated to a dull red by a 2-volt accumulator with adjustable resistance in series.

Fig. 3.

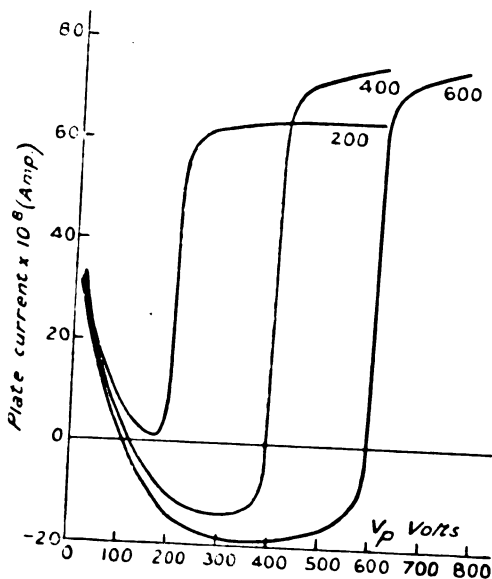


The grid was raised to a fixed potential V_G by a battery of small accumulators, and the plate maintained at various potentials V_P by the same accumulators. The negative pole of this battery was attached to the negative end of the filament, and in all cases V_G and V_P represent the potentials measured from this end. The voltage-drop down the filament was generally about 1 volt, and the potentials of grid and plate above the most active portion of the filament—the middle—are .5 volt less than V_G and V_P respectively. For the lower-plate voltages a potentiometer was used.

The plate currents were measured by a sensitive d'Arsonval galvanometer G . In some of the earlier experiments, resistances of about 50,000 ohms were inserted in both the plate and grid leads, as it was feared that the unstable characteristic would give rise to oscillations. Even with this resistance it was found that short-wave oscillations arose with the larger filament emissions, which were revealed by the galvanometer deflexion becoming unsteady, but with very low filament emissions there were no oscillations. In

the final experiments the resistances were not used, and the emission current did not exceed 10^{-6} ampere. It was found an advantage to connect the case of the galvanometer to one of the terminals, as otherwise for the higher potentials the electrostatic forces affected the moving coil. Three of the curves thus obtained connecting the plate current with the plate potential are given in fig. 4, the fixed grid potentials being 200, 400, and 600 volts respectively.

Fig. 4.



Unless the curves are drawn very large, the early parts are not easily distinguishable, and the first portions are therefore shown separately on a different scale and for a rather smaller emission in fig. 5.

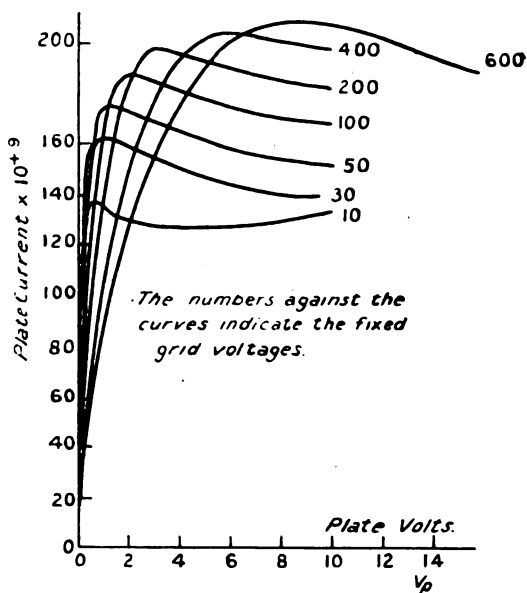
This last figure also contains the first part of curves corresponding to lower grid voltages from 100 to 10 volts. All the curves shown in fig. 5 were determined for me by Mr. C. W. Carter, Rhodes Scholar of Wadham College, Oxford.

It was noticed, as Hull had found, that an increase in the number of electrons leaving the filament over a reasonable range (provided that no oscillations occurred) merely increased the ordinates of all the curves in the same proportion. This is of importance as indicating that the

curves cannot be explained by a large saturation voltage being necessary between grid and plate to collect the secondary electrons on the grid.

3. All the curves taken on the above valve and others of various types showed the same general form as Hull's and Horton's. As V_P is increased from zero, there is a rapid rise in current to a maximum followed by a falling-off to a minimum, then a second rapid rise, and finally a slow

Fig. 5.



approach to a constant value. It will be noticed that the potential V_P which corresponds to the first maximum value of the plate current depends on the grid potential V_G , and increases as V_G is increased; also that the slope of the downward portions vary slightly, becoming steeper as V_G is increased, the successive curves dropping lower and lower. For V_G 400 and 600 the plate current reverses for certain ranges of V_P , showing that more electrons leave the plate than hit it. The final steep rise of current with V_P commences just before the plate potential reaches the same potential as the grid.

A separate experiment showed that any effects of radiation falling on the plate or of ionization of the trace of

residual gas were of the order of 10^{-6} of the effects measured, and are therefore negligible; and the downward bends of the curves can only be due to secondary emission, which in turn depends on the velocity of impact—i.e., on V_P and not on V_G . It is necessary, therefore, to explain why it is that the curves do not, as might be expected, commence to bend down for the same values of V_P , whatever the value of V_G ; also as it is probable that in the experiments giving the curves in fig. 4 the number of primary electrons hitting the plate is approximately the same for the three values of V_G , it might be expected that the dropping portions of the curves should coincide, as the secondary emissions for a particular value of V_P should be the same.

Even if the numbers of electrons hitting the plate are not quite the same for the different values of V_G , it might be supposed that by multiplying the ordinates of one curve by a constant factor it would coincide with one of the other curves; but the figures plainly show this is not the case for the parts of the curves in question.

The discrepancy can be seen in another way. For $V_G=600$ the plate current is zero—that is, one impacting electron on the average sets free one secondary for a velocity given by $V_P=104$; and this is true for a considerable variation of the filament heating and consequent variation of the number of electrons impinging on the plate. For $V_G=400$ this equality is not obtained till $V_P=116$. Thus a marked difference is obtained where it might be supposed that the results would be the same.

4. A satisfactory explanation of the relative shapes of the curves may be obtained by considering the paths of the electrons in the valve. Omitting at first the complication due to the voltage drop down the filament and the distribution of velocities of emission from the filament consider the motion of a stream of electrons leaving the filament with zero velocity, the grid being at potential $+V_G$ and the filament and plate at zero potential. These electrons are accelerated up to the grid, where a portion are collected and the remainder pass through. After passing the grid the force on them is reversed, and if they all moved in straight lines they would just reach the plate with zero velocity. In actual practice the paths are not straight, for as they pass through the grid-spaces they get bent to varying degrees. The force near the very thin grid wires is comparatively large, and the electrons passing through this region are

considerably deflected, while the few which pass through the centre of the grid opening are undeflected.

The retarding force acting on the electrons after they pass the grid bends their paths more and more, with the result that they nearly all return to the grid along curved paths. At the point on their orbit which is furthest from the grid—that is, the turning point—they still have velocity; and if for a particular electron this velocity is equivalent to that due to a fall through a potential difference v_0 , the electron gets as far as the equipotential surface v_0 , and would require a superposed potential v_0 to take it to the plate.

The electrons thus turn at various distances from the plate, those which passed nearest to the grid wires turning at the furthest distance from the plate. Let v be the potential at the points where the latter begin to return to the plate. If the plate potential be gradually raised from zero, the number of electrons reaching the plate will increase rapidly at first, and then slower and slower till the plate potential reaches v , when the plate receives all the electrons which enter the space between the grid and the plate.

After attaining the potential v , the number of electrons reaching the plate remains constant for a considerable increase of V_P above this value.

The actual value of this voltage v depends on V_G ; and, although there is no exact proportionality, it is obvious that if V_G is increased, v is also increased, and a larger voltage is necessary to bring all the electrons to the plate.

Thus the primary current to the plate through the valve for a fixed grid potential rises from zero to a saturation value as V_P is increased from zero to v ; the value of v at which the current becomes constant is dependent on V_G being increased if V_G is increased. This primary current is, however, not shown by the curves obtained in practice, as it is only possible to measure the net current received by the plate—i. e., the primary current less any secondary emission current.

The result of these considerations can be best seen by a study of the curves of fig. 5.

For a low value of the grid voltage such as 10 volts a small value of V_P , probably about 1 volt, is sufficient to cause all the electrons which pass through the grid to reach the plate. A further increase of V_P does not affect the number which reach the plate; and hence, if there were no secondary emission, the current should remain constant when V_P is increased above about 1 volt.

The current in actual fact begins to decrease, and for 1.5 volts is less than for 1 volt, indicating that secondary emission has become appreciable when the primary electron falls through 1.5 volts. The number of secondaries is here only a small fraction of the number of primaries.

This curve thus proves that secondary electrons are being given off for $V_P = 1.5$ volts; and as the emission depends only on the velocity of impact, there must be a secondary emission for $V_P = 1.5$ whatever the value of V_G .

The plate currents for the higher values of V_G do not, however, show any signs of decreasing just after V_P reaches 1 volt. Thus for $V_G = 100$ the current increases till $V_P = 2$, for $V_G = 400$ till $V_P = 6$, and for $V_G = 600$ till $V_P = 9$.

In all these cases the secondary emission which we know exists for $V_P = 1.5$ does not reveal itself in the curve, because for the larger grid voltages $V_P = 1.5$ does not bring all the primary electrons which passed the grid to the plate.

Thus as V_P is increased beyond 1.5, more primaries reach the plate, and the current continues to grow because the increase in the number of primaries collected more than compensates for the secondaries leaving the plate. The experiments show that as V_G is increased, the value of V_P necessary to bring all the primaries to the plate is also increased.

The argument of Horton and Miss Davies that because, with their particular grid voltage, the plate current did not decrease till V_P reached 11 volts therefore secondary emission requires the primary to have a minimum voltage drop of 11, is plainly incorrect as it is impossible to maintain that secondary emission only begins when the plate current begins to decrease.

It is also impossible to maintain that just before 11 volts electrons are reflected from the plate as indicated by the "nearly flat portion of the curve," for each curve in fig. 5 has a nearly flat portion, each for different ranges of V_P .

The general idea that the primary stream is undeflected in passing through a grid of fine mesh is erroneous, especially as a fine mesh is generally composed of very fine wire. This was confirmed by some experiments with another Marconi valve in which the grid had a much finer mesh. With this valve for $V_G = 200$ the plate potential at which the current began to diminish was about 8 volts as compared with 3 volts for the M.T. 5 valve with which the curves in fig. 5 were obtained. It might also be remarked that the curving of the paths of the electrons and the phenomena

resulting therefrom will not be eliminated by increasing the number of grids or by putting in slits near the filament.

The voltage drop down the filament, the distribution of the velocities of the electrons emitted from the filament about their mean values, and contact differences of potential do not affect the general form of the curves to be expected from the simple theory; but it would be necessary to take these effects into consideration in order to estimate the lowest potentials at which the various phenomena may begin to be noticeable.

5. The slight difference in the shapes of the various curves over the portions where the plate current diminishes as the plate potential increases may also be explained by considering the curvature of the paths of the electrons.

Over this region all the primary electrons passing the grid hit the plate. For any particular value of V_G as V_P is increased the retarding force on the electrons after they have passed the grid decreases, which means that the average incidence of the electrons on the plate is most oblique for the low values of V_P and becomes more normal as V_P is increased. To compare the different curves it is best, however, to consider a fixed velocity of impact, that is a fixed value of the plate potential, when by calculating mathematically the effect of varying V_G it can be shown that the higher the value of V_G the more oblique the incidence.

This last fact affords a clue to the apparent non-correspondence of the curves. It has been known for a long time that the number of secondary electrons emitted depends on the angle of incidence of the primary electrons * being a minimum for normal incidence and increasing at any rate initially as the angle becomes more oblique. Thus as V_P is increased, we should expect the curve for $V_G=400$ to drop more steeply than that for $V_G=200$, since an increase of V_P leaves the incidence more oblique in the first than in the second, and the emission thus increases more for the first than for the second. The curves agree with this. Or, if it is preferable to study the points where the curves cut the V_P axis, agreement is also found.

Thus for $V_G=400$ if $V_P=116$, each primary electron which hits the plate with a velocity corresponding to a drop through 116 volts on the average produces one secondary. For $V_G=600$ and more oblique incidence, if $V_P=116$ each primary on the average produces more than one secondary, and V_P need only be 104 to get an average of one. Higher

* *Electricity in Gases*, p. 457 (1915).

values of V_G reduce the value of V_P necessary for equality of incidence and emission still further.

6. The final rise of the curves when V_P approaches the value of V_G indicates that the effect of secondary emission is becoming less. This does not mean that the number of secondaries given off decreases, but that the number of them which reach the grid decreases. Thus in fig. 4 when $V_G=200$ the curve rises after V_P reaches 170 approximately, but the other curves for $V_G=400$ and 600 show that as V_P is increased from 170 to 200 the emission also increases, and the rise of the curve for $V_G=200$ can therefore only be due to some of the secondary electrons returning to the plate and not escaping to the grid; the proportion returning increasing as V_P is increased till, for the higher values of V_P , they all return, and secondary emission has no effect. The simple idea underlying the explanation of Horton and Miss Davies that the field between the grid and the plate is determined solely by the potentials of the grid and the plate, is quite unable to explain this rise; for in all cases the rise begins when V_P is less than V_G —that is, when the field, if due to V_G and V_P alone, would certainly remove the secondary electrons to the grid. (Careful experiments with widely varying currents showed that it is only when V_P is very close in value to V_G that the space-charge round the plate has any appreciable effect.)

The difficulty about the early rise is evaded by Horton and Miss Davies, who remark about the rise in their curve after $V_P=22$ (V_G being 27) that this “indicates that the number of electrons leaving the collecting electrode begins to decrease, causing the resultant negative current to increase,” no reason being given why the number leaving does not decrease. The solution of the difficulty is to be found by a more careful examination of the electric fields.

Starting with the case when the plate and filament are both at zero potential and the grid is at potential V_G , the potential at points in the grid squares drops off as we leave the grid wires, and gets to a minimum at the centre of the square.

It is not necessary for present purposes to attempt the calculation of the variation of the potential across the grid spaces for cylindrical electrodes and grid wires of circular cross-section, but it appears that owing to the large force just outside thin charged wires this variation may be considerable.

Thus when the filament and plate are at zero potential and

the grid at potential V_G , the field is not uniform near the grid, but it is uniform near the plate.

If the plate potential V_P is now raised, V_G being fixed, the field near the plate weakens *, and a mathematical investigation shows that this field becomes zero and reverses for values of V_P less than V_G .

This can also be seen as follows :—When V_P and V_G are equal and the filament is at zero potential, the majority of the lines of force leaving the filament go to the grid, but a few go to the plate ; no others exist, as none can go from the grid to the plate, and hence the force near the plate attracts electrons to it. Hence a reversal must take place before the plate potential becomes equal to that of the grid.

The secondary electrons are emitted with small velocities of various magnitudes ; and therefore as the attractive force on electrons at the surface of the plate increases with V_P , less and less of them get free from the plate, so that the plate current begins to increase a little before V_P reaches the same value as V_G . The secondary emission finally has no effect on the plate current when V_P reaches such a value that the field prevents the fastest secondaries leaving the plate.

The final value to which the plate current approaches as V_P is increased depends on another factor. It will be noticed that the final value of the plate current obtained by increasing V_P is considerably larger than the plate current at its first maximum.

But the current at the first maximum is very approximately equal to the current carried by all the electrons which pass through the grid for the particular value of V_P which gives this maximum since the secondary effect for these low voltages is small.

It is thus evident that as V_P is increased, the proportion of the electrons leaving the filament which pass through the grid increases—that is, the primary current to the plate increases at the expense of the primary current to the grid. (This, of course, could not be the case if it were assumed that the grid acts as a perfect shield and the potential of the plate has no effect on the field between filament and grid.)

Apart, therefore, from any effect of secondary emission, the growth of the plate current as V_P is increased depends on the rate at which the plate robs the grid of its current, and this depends on the dimensions of the parts of the valve.

* The equipotentials for a similar case were worked out by Maxwell (*Electricity and Magnetism*, vol. I. Art. 203 and fig. xiii.).

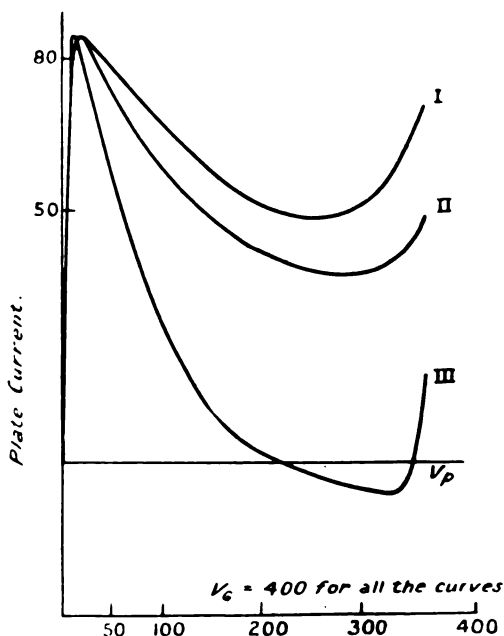
The shape of the curve for the larger values of V_p depends, therefore, both on the elimination of the effect of secondary emission and the diminution of the grid current.

Horton and Miss Davies only allowed for the former in their explanation of this part of the curve, and their estimate of 9 volts as the equivalent velocity of emission of the fastest secondary electron is therefore unreliable, and its agreement with the results of Lenard and others must have been accidental.

It is somewhat difficult to state the values of the plate potentials for which the curves shown in fig. 4 may be said to attain saturation, but these potentials are certainly more than 20 volts above the corresponding grid potentials.

7. The importance of the angle of impact upon the emission is well shown in the curves of fig. 6, which

Fig. 6.



represent the curves taken on three valves—I, II, and III, V_g being 400 for each. These valves were larger than the M.T. 5 valve, and were all very similar in dimensions, except

that the plate of III, though a cylinder of the same average diameter as I and II, was corrugated. The electrons would thus on the average hit the plate of III at a more oblique angle than in I and II. (The grids of these valves were very open, so that in I and II the majority of impacts were nearly normal and the emission less than in fig. 4.)

The currents were measured with both the valves I and II to make certain that small differences in the dimensions of two similar valves did not affect the curves very much.

Curve III shows the much higher emission from the corrugated plate.

8. The explanations given appear to be in satisfactory agreement with the experiments, and the general conclusions may be stated as follows:—

When V_G is large and V_P small, the filament being at zero, it is legitimate to regard the spaces from filament to grid and from grid to plate as being two independent fields; the first determined by the potential difference between filament and grid, the second by that between grid and plate. The electrons entering this latter space enter at various (small) angles to the normal at the point of entry, and the retarding force causes them to move in curved orbits. There are two consequences of this: the first that V_P must reach a certain value before all the primary electrons hit the plate, which causes the plate current to increase with V_P for a bit after secondary emission has commenced; the second that the electrons hit the plate at various angles. The magnitude of both of these effects depends on V_G in a way which can be qualitatively but not quantitatively estimated.

As V_P is further increased, the secondary emission depends not only on the velocity of impact, *i. e.* on V_P , but also on the angle of impact which depends on V_G .

Other considerations come in when V_P approaches V_G in value, and there is very considerable interpenetration of the fields on the two sides of the grid. The field near the plate reverses, and tends to stop the escape of secondary electrons before V_P attains the value of V_G . The effect of secondary emission begins to decrease from this point till, when V_P is sufficiently high above V_G , the velocities of emission of the secondary electrons are not sufficient to prevent them returning to the plate, and secondary emission has no effect on the plate current. It is not, however, possible to determine accurately the point at which the effect of

secondary emission becomes negligible, as the growth of the plate current with increasing V_P is also influenced by electrons which for lower values of V_P went direct from the filament to the grid, being diverted from the grid to the plate.

Owing, therefore, to the number of primary electrons reaching the plate for any value of V_P not being accurately known, and as moreover the angles at which they hit the plate cannot be determined, the curves do not give any precise measurements of the magnitude of secondary emission for definite velocities and angles of impact.

They do show roughly, however, that as the velocity of impact is increased, the number of secondaries emitted for a given number of primaries increases with the velocity of impact, and that the increase continues further if the impact is made more oblique.

The velocity of impact at which secondary emission first became apparent is reduced by reducing V_G ; and even allowing for the velocity of emission of the primary from the filament and contact differences of potential, it seems that there is secondary emission (or reflexion) when the primary drops through one volt or less.

I am indebted to Mr. F. B. Pidduck for some information concerning the electrostatic fields, and to Professor Townsend, in whose laboratory the experiments were made, for much useful advice and criticism.

Note.—The variation of potential over the grid spaces referred to in paragraph 6 appears to have been overlooked by certain experimenters: and a variation will still exist however many grids are employed, and it is not easy to see the validity of the claim sometimes made to fix ionizing and radiating potentials to $\frac{1}{100}$ of a volt when the electrons producing the effect pass through a grid. These values are obtained from the grid potentials as if all the electrons passed through an identical field, whereas, in fact, the majority of them pass the grid at points whose potential certainly differs from that of the grid by more than $\frac{1}{100}$ of a volt.

LXXXIX. *On Ionic Oscillations in the Striated Glow Discharge.* By E. V. APPLETON, M.A., D.Sc., and A. G. D. WEST, B.A., B.Sc., *Denman Baynes Research Student, Clare College, Cambridge* *.

(Published by permission of the Radio Research Board.)

IN the course of some experiments on the electrical properties of ionized gases for high-frequency electromotive forces, it was found that the ordinary striated glow discharge was more often than not a generator of electric waves. The production of such waves indicates that the discharge is not steady, as is usually supposed, but is actually pulsating in character. The presence of the waves may be detected by the ordinary wireless receiving devices, and most conveniently by an auto-heterodyne triode receiver, by means of which it may be shown that the frequency of the oscillations is independent of the electrical constants of the circuit external to the discharge-tube.

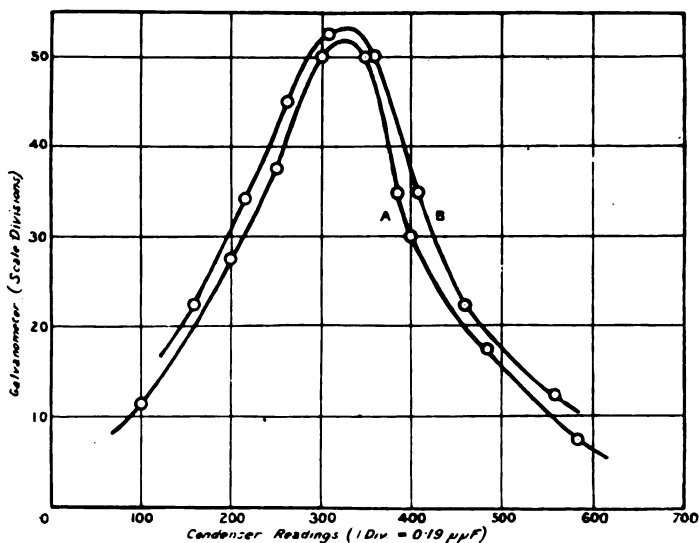
The discharge-tube used was of the simplest type, the diameter being 3·7 cm. and the distance between the electrodes 22 cm. The cathode used in the first instance was of heated platinum (lime-coated), though later experiments showed that a cold cathode will answer quite as well. When a hot cathode was used the anode potential was normally 80–120 volts, but this was increased to 600–800 volts in the case of a cold cathode. In both cases the discharge had to be started by an induction-coil. The anode current was usually of the order of a few milliamperes. When a hot cathode was used the pressure in the discharge-tube was about 0·005 mm. of mercury, but this was increased to 0·25 mm. when the cathode was cold. The number of striations in the tube was adjusted either by altering the gas-pressure or anode potential or by drawing out the striations with a magnet. Oscillations seemed to be most easily obtained when the induction-coil discharge had continued for some time before the steady anode potential was applied. Their production also seemed to depend in some way on the presence of a small glow at the surface of the anode. A noticeable flickering of this glow was found to accompany instability of the discharge.

The ionic oscillations have been detected in three ways, each of which seems to have certain points of interest. In the first method a condenser consisting of two curved tin-foil plates was attached to the outside of the discharge-tube, and also connected in parallel with the condenser of an

* Communicated by Prof. Sir E. Rutherford, F.R.S.

auto-heterodyne receiver. Combination tones of the usual type were heard when the triode-receiver frequency was sufficiently near the frequency of the ionic oscillations of the discharge. The various harmonics of the ionic oscillations were also observed and identified. It was, however, noticed that the note of the combination tone was often not as pure as that heard in the reception of continuous waves from arc or triode generators. In cases when the note was not pure the effect in the telephone can perhaps best be described as being similar to a continuous-wave signal superposed on a background of "atmospherics." Such impurities in the combination tone led us to adopt the second method of detection, in the hope of ascertaining how far from sinusoidal the oscillations were. An oscillatory circuit was fitted up with a diode rectifier and galvanometer

Fig. 1.



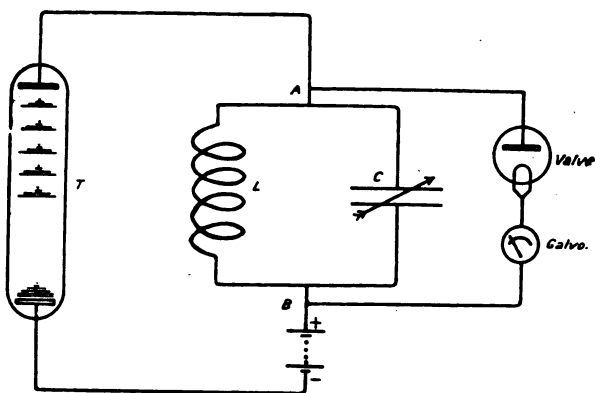
connected in series across the condenser, and the whole placed close to the discharge-tube. A "resonance curve" was obtained for the ionic oscillations and compared with that for a sine-wave generator (triode). These curves are shown as A and B respectively in fig. 1, and it is evident from their similarity that the minor discharges which give rise to the "atmospherics" mentioned above are small compared with the main continuous oscillation.

It is of interest to ascertain whether this method of generating electric waves is to be classed with any of the

known methods. At first sight an analogy with the arc or dynatron is suggested, but it was found that the frequency of the discharge-tube oscillations was independent of the electrical constants of the external circuit. The oscillations are therefore of a new type, being ionic in character and origin.

To illustrate the fact that the frequency of the oscillations was uniquely determined by the internal characteristics of the discharge, an oscillatory circuit was introduced in the anode circuit of the tube, as shown in fig. 2. A diode

Fig. 2.



and galvanometer were used for detecting any oscillatory potential between the points A and B. On gradually increasing the capacity, it was found that for one particular value a large deflexion of the galvanometer was obtained. It is obvious that this happened when the oscillatory circuit LC resonated to the frequency of the oscillations generated in the discharge. Usually the frequencies were of the order of 10^6 per second corresponding to wave-lengths of 2000 to 4000 metres, but in isolated cases frequencies as low as 10^3 have been observed.

In the particular tube we used, the conditions most favourable for the production of oscillations were those in which three or four complete striations were present. We have not made a detailed examination of the dependence of frequency on gas-pressure and anode potential, but have noted that the frequency usually increases with increase of pressure and also with increase of anode potential.

Cavendish Laboratory, Cambridge.
December 1922.

XC. An Investigation of the Structure of the Halogen Salts based on their Compressibility. By IDA WOODWARD*.

THE halogen salts crystallize in the cubic system, the atoms of the alkali metals and those of the halogens being arranged alternately at the corners of the cubes. The following calculations are based on the hypothesis (Sir J. J. Thomson, Phil. Mag. Oct. 1922, p. 662) that the octet of the halogen is completed by the single electron from the outermost shell of the alkali, and that these eight electrons lie at the corners of a cube, which from considerations of symmetry has its edges parallel to those of the cube of the crystal lattice.

Let a be the distance between two adjacent atoms, and $2y$ the edge of the cube of electrons. Then the potential energy per unit volume is a function of a and y , say $f(a, y)$. The condition for the equilibrium of the system is that $f(a, y)$ shall be a minimum for small changes in a and y .

$$\text{That is,} \quad \frac{\partial f}{\partial a} = 0 \quad \text{and} \quad \frac{\partial f}{\partial y} = 0.$$

$$\text{Hence} \quad \frac{df}{da} = \frac{\partial f}{\partial a} + \frac{dy}{da} \cdot \frac{\partial f}{\partial y} = 0.$$

Now the work required per unit volume to compress the crystal so that a is changed to $a - \Delta a$ is

$$\begin{aligned} \frac{df}{da} \cdot \Delta a + \frac{1}{2} \cdot \frac{d^2 f}{da^2} \cdot (\Delta a)^2 + \dots \\ = \frac{1}{2} \cdot \frac{d^2 f}{da^2} \cdot (\Delta a)^2 + \dots \end{aligned}$$

If this changes a volume V to $V - \Delta V$, and C is the compressibility, the work done per unit volume is

$$\frac{1}{2} \cdot \frac{1}{C} \cdot \left(\frac{\Delta V}{V} \right)^2.$$

It is therefore necessary to calculate $\frac{d^2 f}{da^2}$. It will be shown, however, that $\frac{dy}{da}$ is small, so that $\frac{\partial^2 f}{\partial a^2}$ may be substituted for $\frac{d^2 f}{da^2}$ without introducing a large error, since

$$\frac{d^2 f}{da^2} = \frac{\partial^2 f}{\partial a^2} + 2 \cdot \frac{dy}{da} \cdot \frac{\partial^2 f}{\partial y \partial a} + \left(\frac{dy}{da} \right)^2 \cdot \frac{\partial^2 f}{\partial y^2}.$$

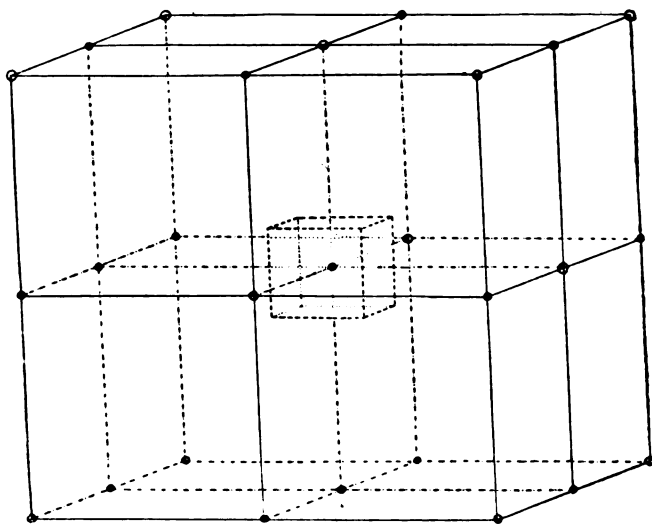
* Communicated by Sir J. J. Thomson, O.M., F.R.S.

The forces acting are assumed to be :

- (i.) a repulsion $\frac{e^2}{r^2}$ between electrons ;
- (ii.) an attraction $\frac{eE}{r^2}$ between a halogen atom and an electron other than those of its own shell ;
- (iii.) an attraction $eE\left(\frac{1}{r^2} - \frac{d}{r^3}\right)$ between a halogen atom and an electron of its own shell ;
- (iv.) an attraction $eE\left(\frac{1}{r^2} - \frac{c}{r^3}\right)$ between an alkali atom and an electron ;
- (v.) a repulsion $EE'\left(\frac{1}{r^2} - \frac{g}{r^3}\right)$ between two atoms ;

where d , c , and g are constants depending on the elements concerned.

Fig. 1.



The diagram (fig. 1) shows a cube of edge $2a$. Halogen atoms lie at the centre of this cube and at the middle points

of the edges. Alkali atoms lie at the corners and at the centres of the faces. The electrons lie at the corners of cubes of edge $2y$ surrounding the halogen atoms. Only one of these cubes is shown in the diagram.

Now, an approximation to the potential energy of the halogen atom lying at the centre of the cube of edge $2a$ is obtained by considering the contribution due to the atoms shown and to the electrons which lie within the cube. Since the atoms at the corners are shared by eight cubes, those at the middle points of the edges by four, and those at the centres of the faces by two, this contribution is

$$\frac{1}{2} \cdot 7e \left\{ \frac{8}{8} \cdot \frac{e}{\sqrt{3}a} + \frac{6}{2} \cdot \frac{e}{a} + \frac{12}{4} \cdot \frac{7e}{\sqrt{2}a} - \frac{G}{a^2} \right. \\ \left. - \frac{8e}{\sqrt{3}y} + \frac{4de}{3y^2} - \frac{24e}{\sqrt{2(a-y)^2 + y^2}} \right\},$$

where $\frac{G}{a^2}$ includes the terms arising from the r^{-3} forces between atoms.

If similar cubes are drawn surrounding an alkali atom and an electron respectively, and the potential energy of these is calculated, it is found that the potential energy of a group consisting of one halogen atom, one alkali atom, and eight electrons is

$$e^2 \times \left[\begin{aligned} & \frac{86.568}{a} - \frac{B}{a^2} - \frac{20.9364}{y} + \frac{9.333}{y^2} \cdot d - \frac{4.6192}{a-y} \\ & + \frac{1.333c}{(a-y)^2} + \frac{8.4864}{a-2y} \\ & + 12 \left\{ \frac{1}{\sqrt{2a^2 + 4y^2}} + \frac{2}{\sqrt{2a^2 + 4ay + 4y^2}} \right. \\ & \quad \left. + \frac{2}{\sqrt{2a^2 - 4ay + 8y^2}} + \frac{1}{\sqrt{2a^2 - 8ay + 12y^2}} \right\} \\ & - \frac{168}{\sqrt{2a^2 - 4ay + 3y^2}} - \frac{24}{\sqrt{a^2 - 2ay + 3y^2}} \\ & \quad \left. + \frac{12c}{a^2 - 2ay + 3y^2} \right] \\ & = U \text{ (say).} \end{aligned} \right] \quad (I.)$$

where B is a constant.

So that $N \cdot U = f(a, y)$, where N is the number of groups per unit volume.

Since the cube of electrons is in equilibrium, $\frac{\partial U}{\partial y} = 0$.
Hence

$$\frac{e^2}{a^2} \times \left[\begin{aligned} & 20.9364 \frac{1}{x^2} - 18.667 \frac{1}{x^3} \cdot \frac{d}{a} - \frac{4.6192}{(1-x)^2} \\ & + \frac{2.667}{(1-x)^3} \cdot \frac{c}{a} + \frac{16.9728}{(1-2x)^2} \\ & + 12 \left\{ \frac{-4x}{(2+4x^2)^{3/2}} + \frac{2(2-4x)}{(2-4x+4x^2)^{3/2}} \right. \\ & \quad \left. + \frac{2(2-8x)}{(2-4x+8x^2)^{3/2}} + \frac{4-12x}{(2-8x+12x^2)^{3/2}} \right\} \\ & - \frac{168(2-3x)}{(2-4x+3x^2)^{3/2}} - \frac{24(1-3x)}{(1-2x+3x^2)^{3/2}} \\ & \quad \left. + \frac{12(2-6x)c}{(1-2x+3x^2)^2} \right] \\ & = 0, \dots \dots \dots \text{(II.)} \end{aligned} \right]$$

where $x = y/a$.

If we evaluate the expression on the left-hand side of this equation for different values of x , we obtain the following set of corresponding values of x , $\frac{d}{a}$, and y .

TABLE I.

x .	d/a .	y .
0	0	...
0.5	0.0554	$d/1.11$
0.75	0.082	$d/1.09$
1	0.108	$d/1.08$
1.25	$0.131 + 0.003 c/a$	$(d - 0.003 c)/1.05$
2	$0.187 + 0.010 c/a$	$(d - 0.010 c)/.93$
2.5	$0.213 + 0.016 c/a$	$(d - 0.016 c)/.852$
3	$0.255 + 0.011 c/a$	$(d - 0.011 c)/.85$

Hence the variation of y with x , and therefore with a , is small, and in calculating the compressibility from $\frac{\partial^2 U}{\partial a^2}$ instead of $\frac{d^2 U}{da^2}$, we shall not be introducing a large error.

Putting $\frac{\partial U}{\partial a} = 0$, since the system is in equilibrium, and eliminating B by means of this equation, we get

$$\frac{\partial^2 U}{\partial a^2} = \frac{e^2}{a^3} \times \left[\begin{aligned} & -86.568 + \frac{13.857}{(1-x)^2} - \frac{9.238}{(1-x)^3} \\ & - \frac{8c}{(1-x)^3 a} + \frac{8c}{(1-x)^4 a} - \frac{25.459}{(1-2x)^2} \\ & + \frac{16.973}{(1-2x)^3} + \frac{336(4-3x)}{(2-4x+3x^2)^{3/2}} \\ & - \frac{504(2-2x)^2}{(2-4x+3x^2)^{5/2}} + \frac{24(4-3x)}{(1-2x+3x^2)^{3/2}} \\ & - \frac{72(1-x)^2}{(1-2x+3x^2)^{5/2}} - \frac{24(4-3x)}{(1-2x+3x^2)^2} \cdot \frac{c}{a} \\ & + \frac{24(2-2x)^2}{(1-2x+3x^2)^2} \cdot \frac{c}{a} \\ & + 12 \left\{ \frac{-8}{(2+4x^2)^{3/2}} - \frac{4(4-3x)}{(2-4x+4x^2)^{3/2}} \right. \\ & - \frac{4(4-3x)}{(2-4x+8x^2)^{3/2}} - \frac{2(4-6x)}{(2-8x+12x^2)^{3/2}} \\ & + \frac{12}{(2+4x^2)^{5/2}} + \frac{24(1-x)^2}{(2-4x+4x^2)^{5/2}} \\ & \left. + \frac{24(1-x)^2}{(2-4x+8x^2)^{5/2}} + \frac{12(1-2x)^2}{(2-8x+12x^2)^{5/2}} \right\} \end{aligned} \right] \\ = \frac{e^2}{a^3} \times A \text{ (say).}$$

The following table gives the value of A for various values of x :—

TABLE II.

x .	A.
0	1.456
.05	0.77 + 4.29 c/a
.075	0.5 + 6.42 c/a
.1	0.29 + 8.29 c/a
.125	0.58 + 9.91 c/a
.2	3.07 + 11.1 c/a
.25	17.2 + 7.42 c/a
.3	73.26 + 0.59 c/a

Employing the method given by Prof. Sir J. J. Thomson (Phil. Mag. April 1922, p. 735) it is found that the work required to compress N groups of 1 halogen atom, 1 alkali atom, and 8 electrons is

$$\frac{1}{2} \cdot N \cdot \frac{A}{9} \cdot \frac{e^2}{a} \cdot \left(\frac{\Delta V}{V} \right)^2,$$

where V is the volume occupied by the N groups. Also if C be the compressibility, the work done per unit volume

$$= \frac{1}{2} \cdot \frac{1}{C} \cdot \left(\frac{\Delta V}{V} \right)^2.$$

Hence
$$A = \frac{9a}{CN e^2},$$

where N is now the number of groups per unit volume.

If M is the mass of one group and Δ the density, $NM = \Delta$ and $N \cdot 2a^3 = 1$.

Therefore
$$A = \frac{9}{e^2 \cdot C \cdot (2)^{1/3}} \cdot \left(\frac{M}{\Delta} \right)^{4/3}.$$

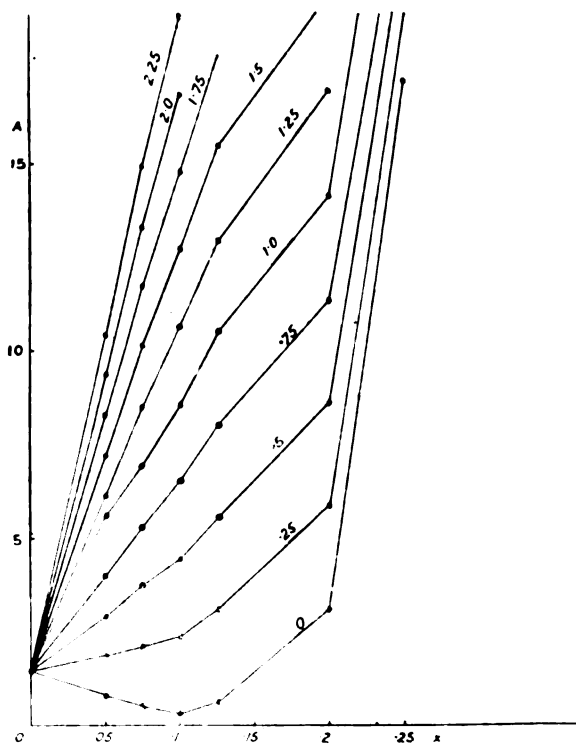
The values of A , calculated from the experimental values for the compressibilities of the six following salts (T. W. Richards and G. Jones, Journ. Am. Chem. Soc. xxxi. p. 176), are:

	NaCl.	NaBr.	NaI.	KCl.	KBr.	KI.
A.....	12.32	12.45	12.75	15.61	15.27	14.41

We have to find values of c for Na and K, and values of d for Cl, Br, and I, such that A has the above values for the various salts.

Consider NaCl. From Table II. graphs of (A, x) for different values of c/a were drawn (fig. 2). The intersections of these curves with the line $A = 12.32$ give a set of corresponding values of x and c/a shown in the first two rows of the table below. From the second column of Table I. graphs of $(d/a, x)$ for the same set of values of c/a were also

Fig. 2.

Graph of (A, x) for different values of c/a .

drawn (fig. 3), and from this a set of corresponding values of d/a was determined, as shown in the third row of the table.

$c/a \dots$	0	.25	.5	.75	1.0	1.25	1.5	1.75	2.0	2.25
$x \dots\dots$	.231	.222	.213	.204	.161	.118	.095	.079	.068	.060
$d/a \dots$	.203	.202	.200	.197	.165	.127	.103	.086	.075	.065

For NaCl, $a=2.817 \text{ \AA}$; so we get the following set of corresponding values of c and d (fig. 4) in Ångström units:—

$c \dots$	0	.704	1.408	2.113	2.817	3.521	4.225	4.930	5.634	6.338
$d \dots$	.5719	.5691	.5634	.5550	.4646	.3577	.2901	.2424	.2141	.1831

Fig. 3.

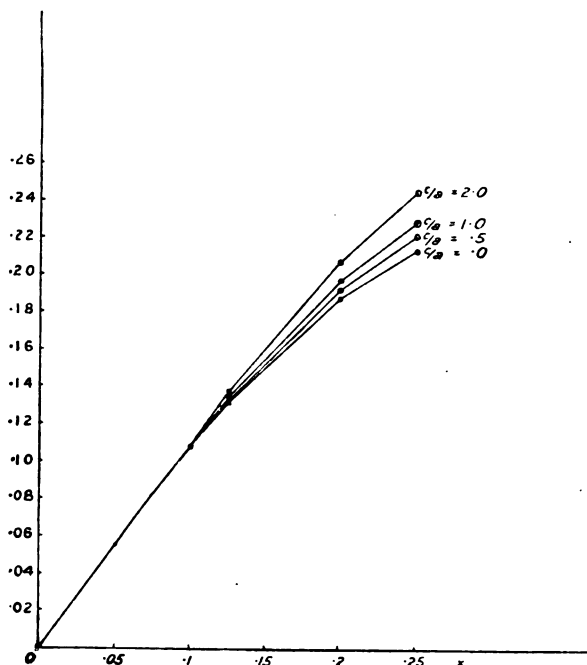
Graph of $(d/a, x)$ for different values of c/a .

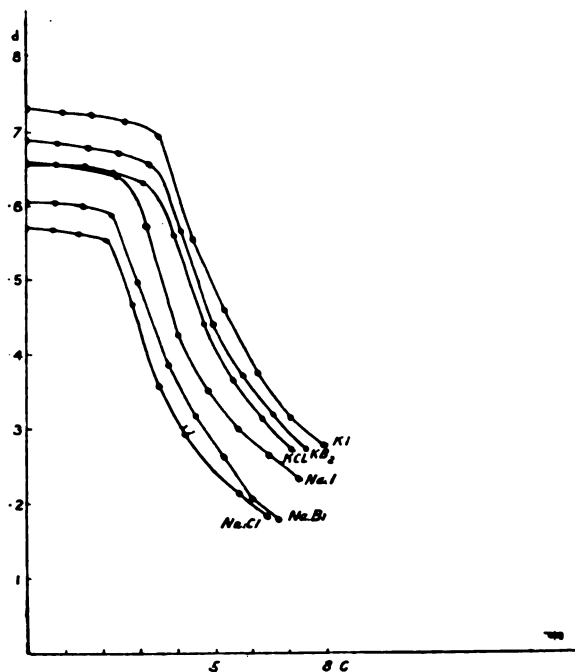
Fig. 4 shows also the graphs of (c, d) obtained in a similar way for NaBr, NaI, KCl, KBr, KI.

If we now take an arbitrary value of c for Na, say 3, we obtain from the curves for NaCl, NaBr, NaI the values .445, .495, .608 of d for Cl, Br, and I respectively. From the curves for KCl, KBr, KI, the values of c for K which correspond to these values of d are seen to be 4.7, 4.56, 4.1. In this way the table given below is drawn up. If the value

c for Na.	d for Cl.	d for Br.	d for I.	c for K given by		
				KCl.	KBr.	KI.
0 Å	.57 Å	.605 Å	.658 Å	3.0 Å	3.8 Å	3.9 Å
1	.567	.603	.657	3.9	3.7	3.9
2	.556	.590	.645	3.95	3.9	4.0
2.5	.510	.570	.640	4.3	4.1	4.0
3	.445	.495	.608	4.7	4.56	4.1
4	.315	.363	.430	6.2	5.9	5.75
5	.236	.277	.334	—	7.2	6.7

assumed for c for Na is the correct one, it is clear that the three values of c for K obtained in this way will be the same.

Fig. 4.

Graph showing relation between c and d .

Hence it is seen that the solution must be in the region

$$\begin{aligned} c &= 0 \text{ to } 2.5 \text{ \AA} \text{ for Na,} \\ c &= 3.8 \text{ \AA} \text{ to } 4.0 \text{ \AA} \text{ for K,} \\ d &= .570 \text{ \AA} \text{ to } .510 \text{ \AA} \text{ for Cl,} \\ d &= .605 \text{ \AA} \text{ to } .57 \text{ \AA} \text{ for Br,} \\ d &= .66 \text{ \AA} \text{ to } .64 \text{ \AA} \text{ for I.} \end{aligned}$$

A method of trial and error readily gives the following values as those of best fit:—

$$\begin{aligned} c \text{ for Na} &= 2.2 \text{ \AA}, \\ c \text{ for K} &= 3.95 \text{ \AA}, \\ d \text{ for Cl} &= .555 \text{ \AA}, \\ d \text{ for Br} &= .590 \text{ \AA}, \\ d \text{ for I} &= .645 \text{ \AA}. \end{aligned}$$

Finally, the compressibility is calculated thus:—

For NaCl, when d and c are $\cdot 555 \text{ \AA}$ and $2\cdot 2 \text{ \AA}$, d/a and c/a are $\cdot 1970$ and $\cdot 7631$ respectively. Hence, from fig. 3, $x = \cdot 231$, and therefore, from fig. 2, $A = 12\cdot 4$. This gives a value $4\cdot 139 \times 10^{-12}$ for the specific compressibility. This process was carried out for all the salts under consideration, and the following values for the compressibility were obtained:—

	Compressibility (calculated).	Compressibility (observed).
NaCl	$4\cdot 139 \times 10^{-12}$	$4\cdot 11 \times 10^{-12}$
NaBr	5\cdot 099	5\cdot 08
NaI	6\cdot 990	6\cdot 9
KCl	5\cdot 061	5\cdot 03
KBr	6\cdot 351	6\cdot 23
KI	8\cdot 660	8\cdot 6

The observed values of the compressibility are taken from the paper quoted above (T. W. Richards and G. Jones, Journ. Am. Chem. Soc. xxxi. p. 176).

The atomic diameters of Cl, Br, and I, as given by Prof. W. L. Bragg (Phil. Mag. August 1920, p. 180), are $2\cdot 10$, $2\cdot 35$, $2\cdot 80 \times 10^{-8} \text{ cm}$.

$$\text{Since } \frac{\cdot 590 - \cdot 555}{\cdot 645 - \cdot 555} = \cdot 39, \text{ and } \frac{2\cdot 38 - 2\cdot 10}{2\cdot 80 - 2\cdot 10} = \cdot 4,$$

the values of d when plotted against the atomic diameters will fall very nearly on a straight line.

As is shown below, the diameter of the cube of electrons surrounding an atom is of the order of the atomic diameter.

	NaCl.	NaBr.	NaI.	KCl.	KBr.	KI.
Diagonal of cube ...	1\cdot 9784	2\cdot 132	2\cdot 354	1\cdot 8904	2\cdot 022	2\cdot 220
Atomic diameter ...	2\cdot 10	2\cdot 38	2\cdot 80	2\cdot 10	2\cdot 38	2\cdot 80
Ratio	\cdot 942	\cdot 896	\cdot 841	\cdot 900	\cdot 858	\cdot 793

Using the values of c to determine the wave-length for the specific photo-electric effect by the method given by Sir J. J. Thomson (Phil. Mag. April 1922, p. 732), we get the following results:—

	λ (calculated).	λ (observed).
Na	3784	3400
K	4216	4400

The above results were applied to the silver salts.

Silver chloride and silver bromide crystallize in a simple cube of edge $2.78 \text{ \AA}$ and $2.89 \text{ \AA}$ respectively, the arrangement of the atoms being the same as in NaCl (Wilsey, Phil. Mag. vol. xlii. p. 262, 1921).

If we suppose that the silver contributes one electron to the chlorine or bromine octet, then, using the values of d just obtained ($0.555 \text{ \AA}$ for Cl and $0.590 \text{ \AA}$ for Br), a calculation similar to that undertaken for NaCl shows that the following values of c for silver give results in agreement with the observed value of the compressibility:—

$$\begin{aligned}\text{For } \text{AgCl}, c &= 4.575 \text{ \AA}; \\ \text{AgBr}, c &= 4.590 \text{ \AA}.\end{aligned}$$

Taking as the mean of these values, c for silver $= 4.580 \text{ \AA}$, the following are the values calculated for the compressibility:—

	Compressibility (calculated).	Compressibility (observed). (T. W. Richards & G. Jones, <i>loc. cit.</i>)
AgCl	2.30×10^{-12}	2.22×10^{-12}
AgBr	2.68 ..	2.59 ..

Specific Inductance Capacity of Salts.

A calculation of the specific inductive capacity of sodium chloride and of potassium chloride was made thus:—

In an electric field X the atoms and electrons in the crystal undergo the following displacements:—

- (i.) The framework of the alkali atoms is displaced relatively to that of the chlorine atoms.
- (ii.) The shells of electrons surrounding the chlorine atoms are displaced relatively to these atoms.
- (iii.) The shells of electrons surrounding the alkali atoms are displaced relatively to these atoms.

Let us consider these effects separately, when the electric field is parallel to the edge of the cube.

(i.) To calculate this effect, regard the atoms as charges $+e$ and $-e$. Suppose the displacement of the lattice of the alkali atoms relative to that of the chlorine atoms is δz .

Then, from the equilibrium of a displaced atom, we have

$$Xe = \frac{14}{3} \cdot \frac{\alpha}{a^4} \cdot e^2 \cdot \delta z,$$

when the attraction between unlike atoms is $\left(\frac{1}{r^2} - \frac{\alpha}{r^3}\right)e^2$ and the effect of the 26 nearest atoms is considered.

To find α , consider the potential energy V of the atom in the absence of the electric field. It is found that

$$V = -e^2 \left(\frac{1.4558}{a} - \frac{3.333}{2a^2} \alpha \right),$$

when a repulsion $\frac{e^2}{r^2}$ is assumed between atoms of the same kind.

For equilibrium, $\frac{\partial V}{\partial a} = 0$; hence $\frac{\alpha}{a} = .4367$.

Now, in unit volume there are $1/2a^3$ atoms of each kind.

Hence the electric moment per unit volume

$$\begin{aligned} &= \delta z \cdot e \cdot /2a^3 \\ &= \frac{3}{28} \cdot X. \end{aligned}$$

This is equal to $\frac{K-1}{4\pi} \cdot X$.

Therefore $\frac{K-1}{4\pi} = .2453$.

(ii.) If we consider the equilibrium of an electron of the outermost shell surrounding the chlorine atom in the displaced condition, we find that the restoring forces exerted by the other atoms on the electron are small compared with the force exerted by the chlorine atom itself, and that the latter is

$$\frac{7e^2 \cdot d \cdot \delta z}{27y^4},$$

where δz is the displacement of the electron relative to the chlorine atom measured in the direction of the field, and d, y are the quantities defined in the earlier part of this paper.

The electric moment per unit volume is therefore

$$\frac{8 \cdot e \cdot \delta z}{2a^3} = \frac{4.27}{7} \cdot \frac{y^4}{da^3} \cdot X.$$

On substituting for y , d , and a , we find

$$\frac{K-1}{4\pi} \text{ for NaCl} = \cdot 133,$$

$$\text{for KCl} = \cdot 080.$$

For the inner shells, y^4 decreases rapidly, and the effect of these shells will be neglected.

(iii.) On performing a calculation similar to the above for the outermost shell of the electron still surrounding the alkali atom, we get

$$\frac{K-1}{4\pi} \text{ for NaCl} = \cdot 0031,$$

$$\text{for KCl} = \cdot 013.$$

The value of the specific inductive capacity, when the types of displacement considered above are taken into account, is:—

For sodium chloride,

$$K = 1 + 4\pi[\cdot 2453 + \cdot 133 + \cdot 0031]$$

$$= 5\cdot 793;$$

and for potassium chloride,

$$K = 1 + 4\pi[\cdot 2453 + \cdot 080 + \cdot 013]$$

$$= 5\cdot 252.$$

The observed values of K are :—

Observed	Starke.	W. Schmidt.	Rubens & Nicols.
NaCl	6·29	5·60	5·18
KCl	4·94	4·75	4·55

The calculated value for NaCl is seen to lie between the extreme observed values, while fair agreement is obtained for KCl.

The values of K (given below) are calculated in the same way. No experimental values are available for comparison in these cases :—

NaBr	$K = 5\cdot 914$
NaI	6·031
KBr	5·289
KI	5·363

Summary.

This paper contains a calculation of the compressibility of certain cubic crystals—namely, the chlorides, bromides, and iodides of sodium and potassium, and the chloride and bromide of silver, and also of the specific inductive capacity of sodium chloride and of potassium chloride. A comparison of the calculated with observed values shows that satisfactory agreement is obtained.

This investigation was suggested by Prof. Sir J. J. Thomson, to whose advice and help its completion is also due. I have pleasure in taking the same opportunity of expressing my thanks to the Department of Scientific and Industrial Research for a grant which enabled the work to be undertaken.

XCI. *The Variation of the Photo-electric Activity of a Potassium ferro-cyanide solution with the Concentration of the solution.* By J. H. J. POOLE, *Sc.D.**

IN the course of some previous experiments on the photo-electric theory of vision, it was observed that an aqueous solution of potassium ferro-cyanide exhibited a pronounced photo-electric effect when illuminated by the light of a carbon arc. It was felt at the time that possibly, by measuring the variation of activity of the solution with concentration, some information as to the origin of the photo-electron in the solution might be obtained. Thus, if we consider any dissolved salt, it is plain that there are three possible sources of the photo-electron, *i. e.*, the positive ion, the negative ion, or the undissociated molecule. It is evident that the shape of the curve connecting the activity of the solution with the concentration will depend on which of these three possible origins is the real one, as the degree of the dissociation of the solute will depend on the concentration. Thus in a general way we should expect that if either the positive or the negative ion were responsible, then the rate of increase of activity with concentration would diminish as the concentration increased, while the reverse would hold if the undissociated molecule only emitted the photo-electron. If, however, one radicle of the salt is photo-electric, whether in the combined or ionized condition, the law connecting the activity with the concentration should be a simple linear one.

* Communicated by Prof. J. Joly, F.R.S.

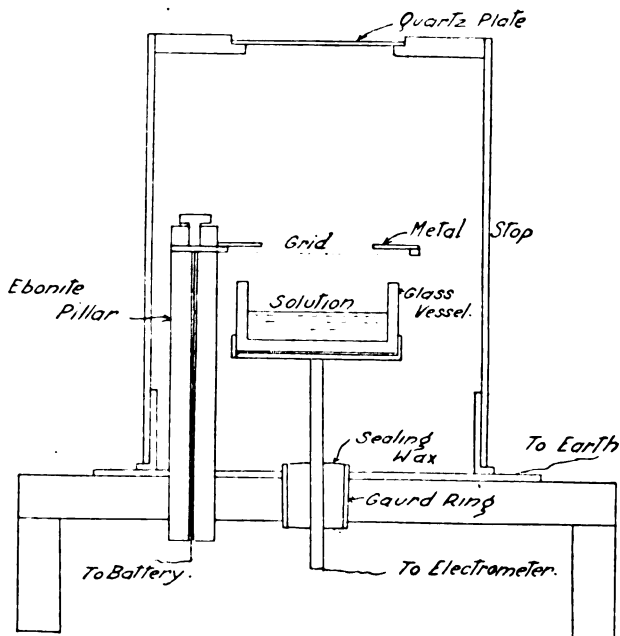
The first attempts at measuring the photo-electric activity of various concentrations were made with a continuous current carbon arc. It was found, however, that consistent results could not be obtained owing to variations in the quantity of ultra-violet light emitted by the arc. Every attempt was made to keep the arc steady by carefully regulating the current through it, but in the end the carbon arc had to be abandoned. It was then decided to use a mercury arc in quartz as a source of light, and after some delay a suitable form of mercury arc was obtained. This arc emitted an approximately constant quantity of ultra-violet light when it had been running for about three-quarters of an hour or more. An ammeter was placed in series with it, so that the current through the arc could be kept constant by means of a regulating resistance.

A Dolezalek quadrant electrometer in conjunction with a special form of ionization vessel was used to measure the electronic current from the solution. The sensitivity of the electrometer could be quickly ascertained by an arrangement by which a known small voltage could be applied to one quadrant. The capacity of the electrometer and ionization vessel was known from previous determinations, and thus the current corresponding to any rate of increase of voltage of the quadrant could be quickly calculated. A sketch of the ionization chamber is shown. The solution to be tested is contained in the glass vessel which fits on top of the central metal platform. The under side of the glass vessel is covered with tinfoil and electrical connexion between this foil and the solution is made by a piece of platinum ribbon which passes over the upper edge of the vessel and dips into the solution. In practice it was found necessary to keep the ribbon slightly greasy where it passed over the edge of the vessel, as otherwise the solution tended to creep out along the ribbon. The metal table on which the glass vessel rests is supported on a central brass pillar which passes through an insulating bushing of sealing-wax in the floor of the ionization chamber. The lower end of this pillar is connected to the isolated quadrant of the electrometer, so that the solution in the glass vessel is directly connected to this quadrant. The advantages of this design are two-fold: firstly, the solution to be tested only comes in contact with glass and platinum and hence we eliminate any effects which might be caused by chemical action between the solution and the containing vessel; and secondly, we can very quickly remove the vessel from the ionization chamber when we desire to substitute a different solution. This point is of

some importance as, owing to possible variations in the intensity of the source of light, it is desirable to be able to test the various solutions as quickly after one another as possible.

To facilitate the escape of the electron from the solution an accelerating electric field was applied in the usual manner to the copper gauze grid fitted, as shown in sketch, over the surface of the solution. This grid was connected to the positive terminal of a high tension battery of about 300 volts

Fig. 1.



pressure. It was found that this voltage was capable of producing approximate saturation in the electronic current even with the strongest solutions. To ensure, however, that no variation in the distance between the surface of the solution and the grid should affect the value of the current, a standard quantity of the solution was always used. Probably at pressures above 300 volts this precaution is not very essential, but at lower pressures the current depended to quite a large extent on the quantity of solution in the glass vessel. This effect was attributed to the fact that the

Phil. Mag. S. 6. Vol. 45. No. 269. May 1923. 3 M

magnitude of the accelerating field will diminish as the quantity of solution is decreased owing to the increased distance between the grid and the solution, and hence unless the field is sufficient to produce the saturation current in any case, the current will fall off with the decrease in quantity of the solution.

It is very necessary in experiments of this nature that it should be quite plain that the photo-electron is really emitted by the solution and not by the solid containing vessel. For this reason the grid was fitted with a stop, which only allowed the light to fall on the central portion of the liquid surface and not on the walls of the vessel. This arrangement will largely reduce the possibility of electrons being emitted by the containing vessel, but there may be still a few emitted owing to scattered light. However, the results show that the effect, if any, must be small, as the activity of pure water when measured in this apparatus is quite small. It is probable that the amount of scattered light would be independent to a large extent of the solution in the vessel, and hence for the stronger solutions the maximum error due to this cause could not exceed the apparent activity of the pure water and would in consequence be a small one. Owing to the fact that it is the rise in voltage of the isolated central vessel that is measured, no error will be caused by a possible emission of electrons by the metallic sides of the ionization vessel, as all such electrons will be attracted to the grid by the electric field. For the same reason no photo-electrons emitted by the grid itself will leak back to the solution.

The top of the ionization chamber is cylindrical and fits over a brass flange fixed to the floor of the chamber, so that it can be quickly removed. The exciting light is admitted through a quartz window in this top. In the earlier experiments a speculum metal mirror was used to direct the light of the mercury arc on to this window, but this mirror was abandoned later on, and the mercury arc arranged to shine directly downwards on the solution. This procedure is not without its objections, but it was found preferable to using the mirror which not only was not a very efficient reflector of ultra-violet light, but also seemed to vary in efficiency owing to possible changes in its polish. To eliminate as far as possible any error due to changes in the relative positions of the ionization vessel and the mercury arc both pieces of apparatus were clamped firmly to the bench, and these clamps never interfered with during the course of the experiments. It was not necessary to tilt

the mercury vapour lamp in order to strike the arc and hence no vibration was caused in starting the lamp. No quartz lenses were used to concentrate the light of the arc on the solution, as the only one of suitable size available seemed rather to decrease than to increase the effect. This was probably due to the lens being too thick and absorbing a large amount of the active shorter wave-lengths in the light beam.

The solutions of potassium ferro-cyanide used were prepared from the pure salt, supplied by Kahlbaum, and distilled water. The water was stored in glass and hence contained a small amount of dissolved impurities. All solid matter was removed from the solution by careful filtration, as the presence of any dust particles in the solution increases its activity very considerably. Thus if a solution is left exposed to the atmosphere for a few hours, and its activity then measured without disturbing the surface, it will be found to be considerably greater than the normal owing to the layer of dust deposited on the solution, and this effect can be removed nearly entirely by stirring up the liquid so as to distribute the dust through it. On this account the solutions after filtration should be exposed to the atmosphere as little as possible, and the solution transferred from its flask to the ionization chamber as quickly as can be arranged. In practice the solution had first to be transferred to a burette so that a known volume might be run into the testing vessel, but the delay caused by this operation is slight, and as it is the lower part of the liquid in the burette which is used, no dust falling on its upper surface is likely to enter the vessel.

The method of conducting an experiment was as follows. The mercury arc was first turned on to allow it to come to a steady state. While the arc was heating up, the electrometer needle was charged, and the sensitivity of the instrument measured. The solution to be tested was then placed in the ionization vessel, and the grid connected to the high tension battery. By this time the arc was probably moderately steady, and the time taken for the electrometer spot of light to move through a known number of scale divisions, when the quadrant was isolated, was noted. A shutter was fitted in the path of the incident beam of ultra-violet light by which the light could be cut off at will. Several readings of the rate of leak were taken, and then the solution was removed from the chamber, a fresh solution inserted and the process repeated.

The chief trouble in these experiments arose from the fact

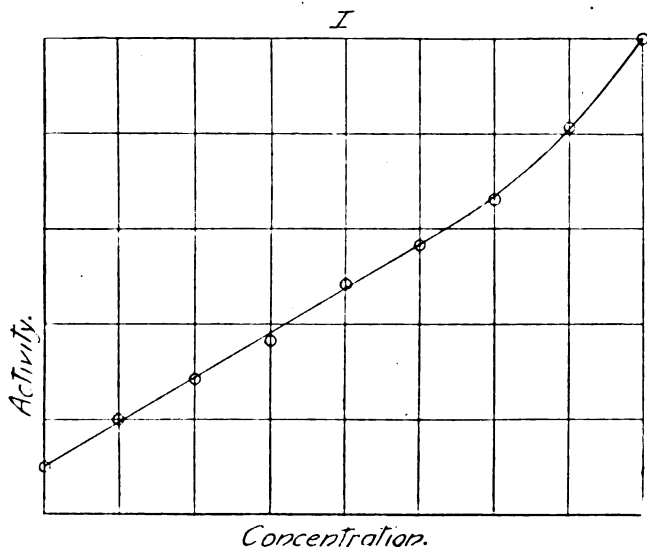
that the mercury lamp was always apparently liable to vary in an erratic manner. As far as the visual light from it was concerned, the arc burnt very steadily, but the amount of ultra-violet light entering the ionization vessel, as measured by the photo-electric discharge from the solution, was not constant. This effect was not due to photo-electric fatigue of the solution, as the activity was as prone to increase with time as to diminish. To eliminate errors due to this cause, the plan adopted was to measure the activity of the strongest solution at frequent intervals during the course of an experiment, and if its value was found to vary by more than about 4 per cent., the readings obtained for the other solutions were neglected.

The table given shows the results of the five most satisfactory series of experiments performed. The number of a solution is simply proportional to its concentration. Solution No. 8 was the strongest solution used and contained 28 gm. of $K_4Fe(CN)_6$ to 100 c.c. of pure water. The other solutions were made up from this solution by dilution with distilled water. As it was found that the activity of the No. 8 solution varied slightly from day to day, owing possibly either to actual variations in the mercury arc itself or to differences in the absorptive power of the air and the quartz window due to differing hygrometric conditions, the activity of this solution has been taken as 100 for each experiment and the activities of the other solutions calculated on this basis. It may be stated that the actual average value of the electronic current per sq. cm. of the strongest solution comes out to be about 8×10^{-14} ampere, or about 5×10^5 electrons per sec. If we assume that a layer only 10^{-8} cm. thick of the solution is affected, this shows that only about one molecule in 10^7 of the potassium ferro-cyanide present in this layer emits an electron every second.

Solution Number.	Activity.					
	I.	II.	III.	IV.	V.	Mean.
8	100	100	100	100	100	100
7	80	82	85	80	78	81
6	62	69	65	72	61	66
5	59	59	51	57	57	57
4	51	48	42	45	53	48
3	37	33	39	34	39	36
2	29	31	29	26	24	28
1	18	19	25	17	19	20
0	4	7	18	11	8	10

The mean value of the activity for each solution has been plotted against the concentration in the following curve. The irregularities in the values of the activity for the various concentrations are probably due to fluctuations in the character of the light, which might not affect a strong and a weak solution in the same way. It is hoped, however, that by taking mean values this error may be eliminated, and the fit of the points on the curve is such as to encourage this view. If we plot the values for any single series of values a curve of similar shape to the main curve is obtained, but usually the observed points do not lie so well on the curve.

Fig. 2.



The curve shows that at the lower concentrations the activity is a simple linear function of the concentration, but that for the stronger solutions the activity increases more rapidly than the concentration. This fact would appear to favour the view that the undissociated molecule is responsible for the photo-electric properties of the solution, but before entering further into this point it may be well to consider briefly whether the range of the photo-electron in the solution itself could have any importance.

Let r = range of electron in solution.

If molecule is in the surface, let the number of electrons

emitted by molecule per second = kI , where I is the intensity of incident illumination. When molecule is at a distance x below the surface, only a fraction of the electrons emitted by the molecule will escape.

To determine this fraction, describe a hemisphere of radius r about the molecule. The ratio of the number of electrons

Fig.3.



escaping from the surface to the number emitted by the molecule may be taken as equal to the ratio of the area of the spherical cap cut off by the surface to the area of the hemisphere. The area of this cap is equal to $2\pi r(r-x)$, hence the value of the fraction escaping will be $\frac{r-x}{r}$.

Let us now consider a layer of area a and thickness dx at a depth x below the surface. Let the number of electrons which escape per second from the liquid and have their origin in this layer be dn . Then we have

$$dn = kI \cdot Na \cdot dx \left(1 - \frac{x}{r}\right),$$

where N = number of molecules of solute per c.c.

and I = intensity of illumination in the layer.

Hence n , the total number of electrons escaping from an area a of the liquid per second, is given by the equation

$$n = \int_0^r kI \cdot Na \left(1 - \frac{x}{r}\right) dx.$$

There are two main cases which may be considered in the solution of this equation. In the first case we may consider that owing to the very small depth of the layer the intensity of illumination will be constant throughout the layer, or secondly, we may assume that this is not true, but that I is a function of the depth and concentration.

Case I.—Let intensity of incident light-beam be I_0 . Then in our expression for n we may write $I = I_0$.

Hence

$$\begin{aligned} n &= kI_0 Na \int_0^r \left(1 - \frac{x}{r}\right) dx. \\ &= kI_0 Na \frac{r}{2}. \end{aligned}$$

This shows that if r , the range of the electron, is independent of the concentration, then the activity of a solution should be simply proportional to the concentration, if the intensity of the light-beam is constant. For the weaker solutions of potassium ferro-cyanide this law seems to be fairly accurately obeyed, but it does not hold for the stronger solutions.

Case II.—If we do not consider the illumination throughout the layer to be constant, the simplest assumption to make is that it will fall off with depth according to an exponential law. Let us accordingly assume that $I = I_0 e^{-\lambda x}$. The value of λ will obviously depend on the concentration, and may be written in the form $\lambda = aN + b$ where a and b are constants, the b term representing the absorption of the solvent. Our expression for n will now become

$$\begin{aligned} n &= k I_0 N a \int_0^r e^{-\lambda x} \left(1 - \frac{x}{r}\right) dx \\ &= k I_0 N a \int_0^r e^{-\lambda x} \left(\frac{x}{\lambda r} + \frac{1}{\lambda^2 r} - \frac{1}{\lambda}\right) dx \\ &= k I_0 N a \left[\frac{1}{\lambda} - \frac{1}{\lambda^2 r} (1 - e^{-\lambda r}) \right] \\ &= k I_0 N a \left[\frac{r}{2} - \frac{\lambda r^3}{3} + \frac{\lambda^2 r^3}{4} - \text{etc.} \right]. \end{aligned}$$

If $\lambda = 0$, that is if we neglect the effect due to absorption, this formula reduces to the one obtained in the previous case. Now λr will always be small, so that we may neglect higher powers of λr than the first. Thus,

$$n = k I_0 N a r \left(\frac{1}{2} - \frac{\lambda r}{3} \right).$$

But

$$\lambda = aN + b.$$

Therefore

$$n = k I_0 N a r \left(\frac{1}{2} - \frac{br}{3} - \frac{aNr}{3} \right).$$

If we consider, as before, that r is independent of N , we may write this equation in the form

$$n = eN(f - gN),$$

where e , f , and g are independent of N .

Differentiating this expression with regard to N , we get

$$\frac{dn}{dN} = e(f - 2gN).$$

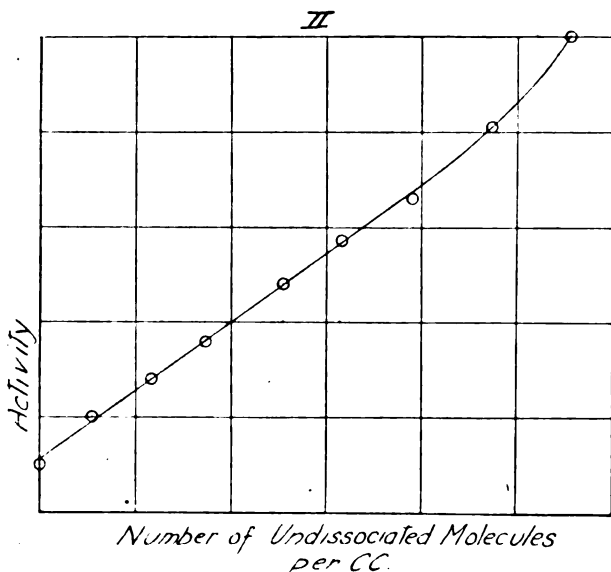
As this shows that the value of $\frac{dn}{dN}$ decreases as we increase the concentration, it entirely fails to explain the experimental results obtained, and accordingly we must look elsewhere for a feasible explanation.

As has already been mentioned, there are three possible sources of the photo-electron in the solution, namely, the positive ion, the negative ion, and the undissociated molecule. The evidence seems, however, to render it very unlikely that the positive ion could be responsible for the photo-electron, as it will already have lost one electron, and is therefore extremely unlikely to lose a second. This view is further confirmed by the fact that potassium ferri-cyanide was found to be nearly entirely inactive in solution, showing that the photo-electric properties must be due to the negative radicle. Previous investigators have also found that the activity of the salts of potassium depends on the negative radicle; thus while potassium chloride decreases the activity of pure water, potassium sulphate increases it considerably. It now remains to be decided whether the negative radicle is active only when not ionized, or whether its state of ionization is immaterial. The possibility that it is only the ionized form that is active may be dismissed, as if this were the case, the slope of the activity curve should decrease with concentration, not increase as the experimental results show it does. The lower linear portion of the curve certainly favours the view that both the negative ion and the undissociated molecule are equally active, but the rapid increase of activity for the stronger solutions is not very easily explained on this hypothesis.

To further investigate this point, the electrical conductivities of the various solutions were measured with a Kohlrausch cell and bridge, and the percentage of undissociated molecules present in each solution calculated from the value of the conductivity for very dilute solutions, on the usual assumption that the change of equivalent conductivity of a solution with concentration is entirely due to the variation in the degree of dissociation of the solute. Curve II. (fig. 4) has been plotted from these results. The abscissæ are proportional to the number of undissociated molecules per c.c. and the ordinates to the activity of the solution. If the activity were due to the undissociated molecules only, and if the chance of a molecule emitting an electron were unaffected by the presence of other molecules of the solute, this curve

would be a straight line. This is not the case, however, as the curve bends decidedly upwards for the higher concentrations, showing that the increase in the number of undissociated molecules is not sufficient to explain the increased activity. There are two possible ways out of this difficulty. One is to suppose that the concentration of the molecules in the surface increases more rapidly for the stronger solutions than the general concentration throughout the liquid. If the surface tension of the solution depends on its strength, we might expect some such effect as this to arise, as in this case

Fig. 4.



the concentration of the solute in the surface layer would be different from the concentration throughout the bulk of the liquid. Dorsey (Phil. Mag. 1897) has shown that in general the surface tension of aqueous salt solutions is greater than that of pure water, and this would lead to the surface layer being poorer in the solute than the rest of the liquid. He also showed, however, that the surface tension of the solution was a simple linear function of the concentration, and this would naturally lead us to suppose that the concentration in

the surface layer was proportional to the general concentration in the liquid, although not equal to it. If this view is correct, we cannot explain the increased activity of the strong solutions on these grounds, and we are forced to turn to the second alternative, namely that the activity of a molecule of the solute is not independent of the presence of other similar molecules, but increases as the concentration is increased. This seems to be a plausible explanation as in many cases it has been found that a body in the solid state is much more photo-electric than in the liquid state. Thus in the very strong solutions we might expect that the solute was not entirely broken up into molecules and ions, but that some of the molecules were still associated into larger groups. As these groups would approximate more closely to the conditions of the solid state, it would be natural to suppose that the activity of the group as a whole would be greater than the sum of the activities of its component molecules when isolated, and hence the increased activity of the stronger solutions would be explained.

Summary of Paper.

Experiments on the variation of the photo-electric activity of a potassium ferro-cyanide solution with concentration are described. It is shown that :—

- (a) The negative radicle is probably responsible for the photo-electric properties of the solution.
- (b) The relative increase of activity of the stronger solutions cannot be accounted for either by the possible effects of the range of the photo-electron in the solution or by the increase in the number of undissociated molecules per c.c. of solution. It seems probable that this increase is to be attributed to the effect of a possible association of the molecules of the solute in the more concentrated solutions.

Physical Laboratory,
Trinity College, Dublin.
February, 1923.

XCH. *On the Velocity of Sound in Liquids contained in Circular Cylinders with slightly Elastic Walls.* By H. G. GREEN, M.A.*

History and aim of the Paper.

EXPERIMENTING in 1847, Wertheim found that the velocity of sound in an organ-pipe completely immersed in water was reduced to 1173 metres per second, and he put forward the theory that the water in the pipe behaved as a quasi-elastic solid. Helmholtz (1848) by a general discussion showed that this theory could not be correct, and suggested that the effect was due to yielding of the pipe-walls, an interpretation supported by Kundt and Lehmann (1874) and by Dvořák in their experiments with water by the method of Kundt's dust tube. We propose to obtain an approximate expression for the velocity on the hypothesis that the change is entirely due to the give of the walls, and to compare results so obtained with those of experiment. This comparison unfortunately can only be rough, from the absence of full data of the pipes employed.

References.

An account of the experiments to be discussed may be found in Barton's 'Sound,' 4th edition. In the treatment of the hollow cylinder, the methods used by Chree (Cambridge Phil. Soc. Trans. vol. xiv. 1889) and Love for the vibrations of solid ones will be followed. Paragraphed references under the latter name are to his 'Mathematical Theory of Elasticity,' 3rd edition. References "G. and M." are to the 'Treatise on Bessel Functions' (Gray and Mathews, 1895), while necessary physical constants are from Landolt-Börnstein's Tables.

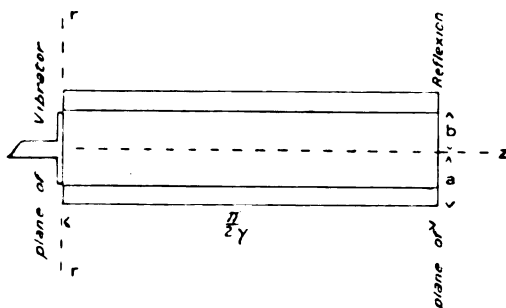
Notation.

The general notation of Love will be adopted, using cylindrical coordinates. The pipe (fig. 1) is to have its axis along the axis of z , and, in the equilibrium state, to have external and internal radii a , b respectively. The length of the sound-wave ($\frac{2\pi}{\gamma}$) is supposed to be large compared with a and b , but the discussion is not confined

* Communicated by Prof. E. H. Barton, F.R.S.

to the case of the "thin-walled" pipe. The plane of reflexion, supposed fixed in space by external agency, is, taken as the plane $z = \frac{\pi}{2\gamma}$.

Fig. 1.



We shall first consider the displacements of the material of the pipe under a radial pressure $P \cos nt \sin \gamma z$ on the inner surface with trial displacements

$$u_r = U \cos nt \sin \gamma z, \quad u_\theta = 0, \quad u_z = W \cos nt \cos \gamma z,$$

where U and W are functions of r . [cf. Love, § 199.]

The equations of motion, as in Love (§§ 199 to 201), reduce to

$$\frac{\partial^2 \Delta}{\partial r^2} + \frac{1}{r} \frac{\partial \Delta}{\partial r} + h^2 \Delta = 0, \quad . \quad . \quad . \quad (1)$$

$$\frac{\partial^2 \varpi_\theta}{\partial r^2} + \frac{1}{r} \frac{\partial \varpi_\theta}{\partial r} - \frac{\varpi_\theta}{r^2} + k^2 \varpi_\theta = 0, \quad . \quad . \quad . \quad (2)$$

where

$$h^2 = n^2 \rho / (\lambda + 2\mu) - \gamma^2, \quad k^2 = n^2 \rho / \mu - \gamma^2,$$

$$\Delta = \frac{1}{r} \frac{\partial (r u_r)}{\partial r} + \frac{\partial u_z}{\partial z},$$

and

$$2\varpi_\theta = \frac{\partial u_r}{\partial z} - \frac{\partial u_z}{\partial r};$$

or

$$\Delta = \left(\frac{\partial U}{\partial r} + \frac{U}{r} - \gamma W \right) \cos nt \sin \gamma z, \quad . \quad . \quad . \quad (3)$$

$$2\varpi_\theta = \left(\gamma U - \frac{\partial W}{\partial r} \right) \cos nt \cos \gamma z. \quad . \quad . \quad . \quad (4)$$

The solutions of equation (1) for Δ are of types $J_0(hr)$, $Y_0(hr)$, and of equation (2) for ϖ_θ of types $J_1(kr)$, $Y_1(kr)$,

and we have to take U and W of the forms

$$U = \frac{\partial}{\partial r} \{A J_0(hr) + B Y_0(hr)\} + \gamma \{C J_1(kr) + D Y_1(kr)\},$$

$$W = \gamma \{A J_0(hr) + B Y_0(hr)\} + \frac{1}{r} \frac{\partial}{\partial r} \{Cr J_1(kr) + Dr Y_1(kr)\}.$$

Using the relations between first derivatives of Bessel functions

$$\frac{\partial}{\partial x} J_0(x) = -J_1(x),$$

$$\frac{\partial}{\partial x} J_1(x) = J_0(x) - \frac{1}{x} J_1(x),$$

or

$$\frac{\partial}{\partial x} x J_1(x) = x J_0(x), \quad . \quad . \quad . \quad . \quad . \quad (5)$$

with similar expressions in the Y 's, [G. and M. pp. 13, 14] these may be re-written

$$U = -h \{A J_1(hr) + B Y_1(hr)\} + \gamma \{C J_1(kr) + D Y_1(kr)\}, \quad (6)$$

$$W = \gamma \{A J_0(hr) + B Y_0(hr)\} + k \{C J_0(kr) + D Y_0(kr)\}, \quad (7)$$

and hence

$$\Delta = -(h^2 + \gamma^2) \{A J_0(hr) + B Y_0(hr)\} \cos nt \sin \gamma z. \quad . \quad . \quad (8)$$

The radial tractive force is given by

$$\widehat{rr} = \lambda \Delta + 2\mu \frac{\partial u_r}{\partial r},$$

and the tractive force parallel to the axis by

$$\widehat{rz} = \mu \left(\frac{\partial u_r}{\partial z} + \frac{\partial u_z}{\partial r} \right);$$

and so by substitution from (6), (7), and (8) we obtain after simplification by (5)

$$\widehat{rr} / \cos nt \sin \gamma z$$

$$\begin{aligned} &= A \left[(-\lambda(h^2 + \gamma^2) - 2\mu h^2) J_0(hr) + \frac{2\mu h}{r} J_1(hr) \right] \\ &+ B \left[(-\lambda(h^2 + \gamma^2) - 2\mu h^2) Y_0(hr) + \frac{2\mu h}{r} Y_1(hr) \right] \\ &+ 2\mu \gamma C \left[k J_0(kr) - \frac{1}{r} J_1(kr) \right] \\ &+ 2\mu \gamma D \left[k Y_0(kr) - \frac{1}{r} Y_1(kr) \right], \quad . \quad . \quad . \quad . \quad (9) \end{aligned}$$

and

$$\begin{aligned} \widehat{rz} / \cos nt \cos \gamma z &= -2\mu \gamma h [A J_1(hr) + B Y_1(hr)] \\ &- \mu (k^2 - \gamma^2) [C J_1(kr) + D Y_1(kr)]. \quad (10) \end{aligned}$$

Now for a modulus x ,

$$J_0 = 1 - \frac{x^2}{4} + \dots,$$

$$J_1 = \frac{x}{2} - \frac{x^3}{16} + \dots,$$

$$Y_0 = J_0 \log x + 4 \left(\frac{J_2}{2} - \frac{J_4}{4} + \dots \right),$$

$$Y_1 = J_1 \log x - \frac{1}{x} - \frac{J_1}{2} + \frac{6 \cdot 3}{2 \cdot 4} J_3 - \dots;$$

[G. and M. p. 22]

and where x is small we can write in (9), (10) to obtain a first approximation, 1 , $\log x$, $\frac{x}{2}$, $-\frac{1}{x}$ for $J_0(x)$, $Y_0(x)$, $J_1(x)$, $Y_1(x)$ respectively (that is, the leading terms in the expansions of the functions), and retaining only the largest terms in the multipliers of A, B, C, and D, we have

$$\begin{aligned} \widehat{r} / \cos nt \sin \gamma z &= -A[\lambda(h^2 + \gamma^2) + \mu h^2] - B \frac{2\mu}{r^2} + C \mu \gamma k + D \frac{2\mu \gamma}{kr^2}, \\ \widehat{r} z / \mu \cos nt \cos \gamma z &= -A \gamma h^2 r + B \frac{2\gamma}{r} - C \frac{(k^2 - \gamma^2)kr}{2} + D \frac{(k^2 - \gamma^2)}{kr}. \end{aligned}$$

We have as boundary conditions:—

$$\text{When } r=b, \quad \widehat{r}r = -P \cos nt \sin \gamma z, \quad \widehat{r}z = 0;$$

$$,, \quad r=a, \quad \widehat{r}r = 0, \quad \widehat{r}z = 0;$$

which give four equations to determine the constants, and lead to, after heavy but straightforward algebra,

$$\frac{A}{\Delta_A} = \frac{-B}{\Delta_B} = \frac{C}{\Delta_C} = \frac{-D}{\Delta_D} = \frac{P}{\Delta_P},$$

where

$$\Delta_A = \mu(k^2 - \gamma^2)(k^2 + \gamma^2) \frac{a^2 - b^2}{a^3 b},$$

$$\Delta_B = (k^2 - \gamma^2) [\lambda(h^2 + \gamma^2)(k^2 - \gamma^2) + \mu h^2(k^2 + \gamma^2)] \frac{a^2 - b^2}{2ab},$$

$$\Delta_C = -\frac{2\mu \gamma h^2}{k} (k^2 + \gamma^2) \frac{a^2 - b^2}{a^3 b},$$

$$\Delta_D = -\gamma k [\lambda(h^2 + \gamma^2)(k^2 - \gamma^2) + \mu h^2(k^2 + \gamma^2)] \frac{a^2 - b^2}{ab},$$

$$\Delta_P = -\mu(k^2 + \gamma^2) [\lambda(h^2 + \gamma^2)(k^2 - \gamma^2) + \mu h^2(k^2 + \gamma^2)] \frac{(a^2 - b^2)^2}{a^2 h^3};$$

also $\lambda(h^2 + \gamma^2)(k^2 - \gamma^2) + \mu h^2(k^2 + \gamma^2)$, which is a factor in three of these expressions, can be re-written as

$$\frac{\lambda n^2 \rho}{\lambda + 2\mu} \left(\frac{n^2 \rho}{\mu} - 2\gamma^2 \right) + \frac{\mu n^2 \rho}{\mu} \left(\frac{n^2 \rho}{\lambda + 2\mu} - \gamma^2 \right),$$

or, after manipulation, as

$$-n^2 \rho \gamma^2 \frac{3\lambda + 2\mu}{\lambda + 2\mu} \left[1 - \frac{v^2}{E/\rho} \right],$$

where $v = n/\gamma$ is the velocity of propagation and $E = \frac{\mu(3\lambda + 2\mu)}{\lambda + \mu}$ is Young's modulus.

[It is to be noted that to our degree of approximation the solution breaks down if $v = \sqrt{\frac{E}{\rho}}$. Cf. Chree's result for a solid cylinder.]

From (6) we have

$$U = \frac{r}{2} [-Ah^2 + C\gamma k] + \frac{1}{r} \left[B - \frac{D\gamma}{k} \right],$$

or

$$\frac{U\Delta_P}{P} = \frac{r}{2} [-\Delta_A h^2 + \Delta_C \gamma k] + \frac{1}{r} \left[-\Delta_B + \frac{\Delta_D \gamma}{k} \right];$$

$$\begin{aligned} -\Delta_A h^2 + \Delta_C \gamma k &= -\frac{a^2 - b^2}{a^3 b} (k^2 + \gamma^2)^2 \mu h^2 \\ &= -\frac{a^2 - b^2}{a^3 b} (k^2 + \gamma^2) \mu \cdot \frac{n^2 \rho}{\mu} \left(\frac{n^2 \rho}{\lambda + 2\mu} - \gamma^2 \right) \\ &= \frac{a^2 - b^2}{a^3 b} (k^2 + \gamma^2) \cdot n^2 \rho \gamma^2 \left(1 - \frac{r^2 \rho}{\lambda + 2\mu} \right), \\ -\Delta_B + \frac{\Delta_D \gamma}{k} &= \frac{a^2 - b^2}{2ab} (k^2 + \gamma^2) n^2 \rho \gamma^2 \cdot \frac{3\lambda + 2\mu}{\lambda + 2\mu} \left(1 - \frac{r^2 \rho}{E/\rho} \right), \end{aligned}$$

and

$$\frac{U}{P} = \frac{b^2}{2(a^2 - b^2)} \left\{ r \frac{\left(1 - \frac{r^2 \rho}{\lambda + 2\mu} \right) (\lambda + 2\mu)}{\left(1 - \frac{r^2 \rho}{E} \right) (3\lambda + 2\mu)} + \frac{a^2}{r} \right\}. \quad (11)$$

We are now in a position to discuss the hydrodynamical problem. It is supposed that the waves remain plane and that the pressure variations are small. The displacements of the walls of the pipes are then small, and we can consider

the hydrodynamical pressure on the inner wall as radial instead of normal.

We can take the radial displacement of the inner wall ($r=b$) as $u_r = U \cos nt \sin \gamma z$ under pressure

$$p = P \cos nt \sin \gamma z, \quad . \quad . \quad . \quad (12)$$

where, in accordance with equation (11),

$$\frac{U}{P} = \frac{b}{2(a^2 - b^2)\mu} \left\{ \frac{b^2 \left(1 - \frac{v^2 \rho}{\lambda + 2\mu}\right) (\lambda + 2\mu)}{\left(1 - \frac{v^2 \rho}{E}\right) (3\lambda + 2\mu)} + a^2 \right\}. \quad (13)$$

Let ξ be the liquid displacement at time t relative to z in space. We shall write δ_0 for the density in the unstrained state and δ for that at time t .

To a first approximation the equation of continuity is

$$\delta \left\{ 1 + \frac{2u_r}{b} \right\} \left(1 + \frac{\partial \xi}{\partial z} \right) = \delta_0, \quad . \quad . \quad . \quad (14)$$

and that of force is

$$-\frac{\partial p}{\partial z} = \delta_0 \frac{\partial^2 \xi}{\partial t^2}. \quad . \quad . \quad . \quad (15)$$

But by (12),

$$u_r = \frac{U}{P} p,$$

and (14) becomes

$$\delta \left\{ 1 + \frac{2U}{bP} p \right\} \left(1 + \frac{\partial \xi}{\partial z} \right) = \delta_0,$$

or say

$$\delta(1 + \alpha p) \left(1 + \frac{\partial \xi}{\partial z} \right) = \delta_0, \\ \text{where } \alpha = \frac{2U}{bP}. \quad . \quad . \quad . \quad (16)$$

But

$$p = K \frac{\delta - \delta_0}{\delta_0} = K \frac{1 - (1 + \alpha p) \left(1 + \frac{\partial \xi}{\partial z} \right)}{(1 + \alpha p) \left(1 + \frac{\partial \xi}{\partial z} \right)}, \text{ from (16),} \\ = -K \left(\alpha p + \frac{\partial \xi}{\partial z} \right) \text{ approx.,}$$

α and $\frac{\partial \xi}{\partial z}$ being small,

$$\text{or } p(1 + \alpha K) = -K \frac{\partial \xi}{\partial z}.$$

Hence

$$\frac{K}{1+\alpha K} \frac{\partial^2 \zeta}{\partial z^2} = \delta_0 \cdot \frac{\partial^2 \zeta}{\partial t^2}, \text{ from (15),}$$

or

$$v^2 = \frac{K}{\delta_0} \frac{1}{1+\alpha K}.$$

If we write $v_0 = \sqrt{\frac{K}{\delta_0}}$ as the velocity of plane waves in liquid of unlimited extent, we have therefore

$$v^2 = \frac{v_0^2}{1+\delta_0 \alpha v_0^2}, \quad (17)$$

or

$$v_0^2 = \frac{v^2}{1-\delta_0 \alpha v^2}, \quad (18)$$

where δ_0 is the density of the liquid and

$$\alpha = \frac{1}{(\alpha^2 - b^2)\mu} \left\{ \frac{b^2 \left(1 - \frac{v^2 \rho}{\lambda + 2\mu}\right) (\lambda + 2\mu)}{\left(1 - \frac{v^2 \rho}{E}\right) (3\lambda + 2\mu)} + a^2 \right\}.$$

The quantity $\delta_0 \alpha v^2$ in equation (18) can be given a direct physical meaning. We shall consider the fluxes through the boundaries of a cylinder of radius b and length δz , with its axis along the axis of z and centre at the point z . The velocity q along the axis is then given by

$$q = -\frac{\gamma P}{n \delta_0} \cdot \sin nt \cos \gamma z.$$

The outward flux through the plane faces is given by

$$\pi b^2 \frac{\partial q}{\partial z} \cdot \delta z = \frac{\pi b^2 \gamma^2 P}{n \delta_0} \cdot \sin nt \sin \gamma z \cdot \delta z,$$

and the inward flux through the curved surfaces by

$$-2\pi b \cdot \delta z \cdot \frac{\partial u_r}{\partial t} = 2\pi b n U \sin nt \sin \gamma z \cdot \delta z,$$

and their ratio

$$= \frac{2n^2 \delta_0 U}{\gamma^2 b P} = \delta_0 \alpha v^2.$$

The assumption that the waves are still appreciably plane demands that this ratio should not be large. In the numerical examples which follow, cases where it exceeds

a half have been rejected as beyond the approximations of the formula.

Where Poisson's ratio is near to a quarter and the value of v is considerably less than $\sqrt{\frac{E}{\rho}}$ (less than half of it is sufficient), the ultimate numerical error in taking $\lambda = \mu = \frac{1}{3}E$, and in neglecting the v^2 term in α , is less than that due to errors in the experimental determinations of the elastic constants. In such cases the approximate value of α is $\frac{(a^2 + \frac{1}{3}b^2)}{(a^2 - b^2)\mu}$.

It may be noted that the relations (17), (18) are independent of the frequency employed. If the expression had been carried to the next approximation, terms containing the frequency would have remained (*cf.* Chree's paper), indicating that for a pipe of given length the overtones are not exact harmonics of the fundamental. Experimental results for elastic constants are not usually very reliable beyond two or three significant figures, and further approximation would not add to the numerical accuracy of the formula.

We will now apply the formula to the experimental cases of Kundt and Lehmann (Table I.) and of Dvořák (Table II.) (see Barton, pp. 533, 535). We shall assume an average glass with $\mu = \lambda = 2.4 \times 10^{11}$ dynes per sq. cm., taking v_0 as 1440 m. per sec. and δ_0 as 1. The differences are given as percentages of the experimental result.

[*Note.*—The possible range for μ is 25 per cent. on either side of the one taken. It probably varied from tube to tube.]

TABLE I.

a in mm.	b in mm.	Temp.	v from Experiment.	v from Formula.	% Diff.
16.55	14.35	18.4	1040.4 (2)	1174	+12.9
20	17	17	1227.7 (3)	1198	- 2.4
14.75	11.75	18	1262.2 (3)	1250	- .97
14	10.5	18.5	1357 (2)	1281	- 5.6
13.25	8.25	18.5	1360 (3)	1328	- 2.4
12	7	22.2	1383 (1)	1339	- 3.2

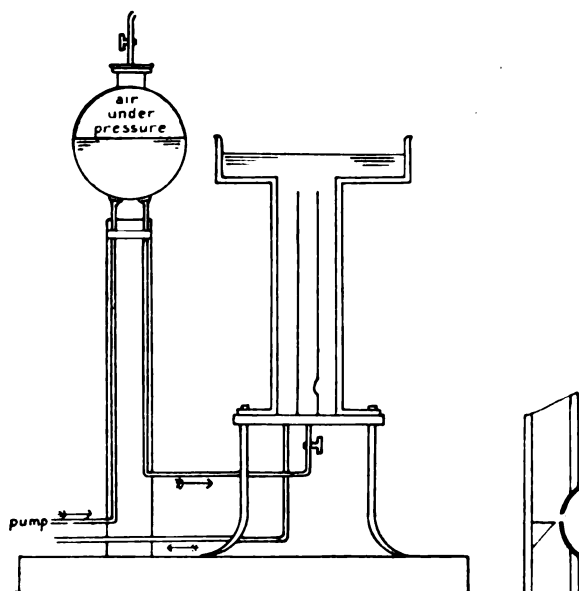
(The experimental results are averages of the numbers of readings indicated in brackets.)

TABLE II.

a in mm.	b in mm.	v from Experiment.	v from Formula.	% Diff.
9.77	8.95	998	1071	+7.3
6.48	5.85	1046	1107	+4.9
4.75	4.23	1164	1133	-2.6
9.5	7.5	1213	1256	+3.5
7.5	5.5	1281	1289	+ .62

Wertheim in 1848 published the results of investigations on the velocities of sound in various liquids, using his organ-pipe method (*Ann. Chim. phys.* (3) xiii. p. 434, 1848).

Fig. 2.



Finding that for Seine water his result when multiplied by $\sqrt{\frac{3}{2}}$ gave very approximately the result for water unlimited in extent, he devised the quasi-elastic theory, and applied the same correction factor to other liquids. Fig. 2 shows the general arrangement of his apparatus,

TABLE III. B.

	Density.	Temp. °C.	v_0 m/s.	$10^6 \times$ compressibility per atmos. cm. ³			v_0 m/s. new theory.
				Cale.	Grassi.	Cale. from new theory.	
Seine water		15	1457	49.1			
Sea-water	1.028	20	1453	46.7	43.6	45.0	1479
Solution NaCl	1.192	18	1561	34.9	32.1	27.8	1750
Solution Na ₂ SO ₄	1.109	20	1525	39.3		34.4	1630
Solution Na ₂ SO ₄	1.160	18.8	1583.5	34.8		27.5	1777
Solution Na ₂ CO ₃	1.183	22.2	1594	33.7	20.7	26.0	1815
Alcohol (common)	.836	20	1285.9	73.3		85.4	1188
Alcohol (abs.)	.796	23	1159.8	94.7	99.1	117.5	1041
Turpentine	.862	24	1212.3	80.0		84.2 ²	1109
Ether	.753	0	1130	100.2	111.0	147 ¹	1635

² From Quincke's results, 1883.¹ From Amagat's results, 1893.

and Table III.A gives his values for $v_0 (= \sqrt[3]{\frac{2}{3}v})$. The agreement of the compressibility deduced from these results with those obtained by Grassi by direct methods (1851) gained the support of Tyndall, in spite of Helmholtz's condemnation. Table III.B gives revised values for v_0 and for the compressibility with, in some cases, the values obtained directly by later experimenters. It will be seen that, except in two cases, the new values show better agreement.

In order to obtain this table we have assumed that $\sqrt[3]{\frac{2}{3}}$ is the correct factor for Seine water, and employed it to obtain the pipe constant. Unfortunately, Wertheim used several tubes and took average results without any regular arrangement, so that the deduced values of v_0 are purely tentative. In any case, the sensitiveness of the formula (18) to slight errors in v renders the method unsatisfactory.

In none of these cases is the formula strictly applicable, for the plane of reflexion is not usually fixed in space, nor is the plane of excitement, as far as the tube is concerned, sufficiently free of external restraint. Difficulty also arises from the radial forces over these planes (*cf.* Love, § 201). In working with the dust tube the experimentalist overcomes these difficulties by using a tube of length an odd number of quarter wave-lengths, taking his measurements only in the central section. In Wertheim's apparatus the movement of the plane of vibration is damped by a quantity of "dead" material (no ordinary fastening is rigid from the point of view of these vibrations), but in those cases where he used an open pipe the conditions at the plane of reflexion are closely approached. The neglect of external variations of pressure in the surrounding medium will produce no error in the formula, for the amplitudes of the vibrations set up are small compared with those of the liquid contained in the tube—they would have to be considered in a second approximation.

Summary.

We have obtained a formula for a certain type of forced vibration in a hollow cylinder, and applied it to find the effects of pipe-yield on sound-waves in a liquid in the cylinder.

On application to various experimental results, it is found that the deduced effect shows agreement which is, on the whole, sufficiently close to confirm Helmholtz's theory and

also to neutralize the agreements which led to support of Wertheim's. It cannot, however, be considered sufficiently close to enable calculation to replace experiment wherever considerable accuracy is required, as it might be, for example, in very long pipe-lines for the Transmission of Power by Waves (method of G. Constantinesco).

University College, Nottingham.
February 1923.

XCIH. *The Effect of Current on the Photo-electric Sensitivity of Metals.* By ALLEN G. SHENSTONE, M.A.*

IN the Philosophical Magazine † I have described certain experiments in which the photo-electric sensitivity of a bismuth plate was temporarily increased by the passage of a current through the plate under examination. Further experiments which have been carried out during the past year have not only confirmed the presence and magnitude of that effect, but have shown it to exist in a number of other metals.

There have recently appeared two very important papers on this subject ‡, Hallwachs and Sende and Simon describe experiments in which a strip of platinum was glowed by means of a current for often repeated intervals of 10 seconds. Readings of photo-electric sensitivity were taken between heatings.

It was found that the photo-electric sensitivity increased very rapidly at first to a high value, from which it decreased more gradually to a value which, in some cases, was too small to be detected by the instruments in use. The authors of the papers base their explanation of this phenomenon on the assumption that the changes of photo-electric sensitivity are entirely due to changes in gas-content of the metal surface. The driving off of the adsorbed surface-layer of gas is made responsible for the rise in photo-electric current by allowing the electrons to escape more easily. Further heating then drives out the absorbed gas, this phase corresponding to the gradual fall of current observed. On this explanation their results lead to the conclusion that gas is essential for the photo-electric emission of electrons from

* Communicated by Prof. E. P. Adams, Ph.D.

† Phil. Mag. xli. p. 916 (1921).

‡ Phys. Zeit. xxi. p. 562 (1920); Ann. der Phys. lxx. p. 697 (1921).

metals. In other words, they do not believe that the photo-electric effect exists at all for pure metals in the range of wave-lengths supplied by a quartz mercury lamp. It is well to point out, however, that their observations were never made on gas-free surfaces, even at the most favourable points in their experiment; for, in a vacuum such as they describe, a metallic surface would be covered by a layer of gas in a very small fraction of a second. This fact renders the authors' explanation of their recuperation curves especially doubtful, since the formation of the surface-layer would prevent the maximum on those curves.

In connexion with those experiments consideration should be given to the work of Millikan * on the effect of temperature on the photo-electric emission from metals. His experiments were carried out in a well-baked-out apparatus, and proved conclusively that between 25° and 125° change of temperature produced no change in the photo-electric emission from copper, gold, nickel, brass, silver, iron, aluminium, magnesium, antimony, zinc, lead. Those experiments covered long periods of time, during which the small changes of temperature used had ample opportunity to produce their maximum effect upon the gas-content of the metals.

The essential difference between the two experiments just described lies in the use by Hallwachs of an electric current through the metal under observation. That the wide divergence of their results and conclusions can be explained by this fact seems probable, from the experiments described by me in *Phil. Mag.* (*loc. cit.*) and from additional work recently carried out. This work indicated distinctly that an electric current can influence the photo-electric sensitivity of a metal directly, independently of its heating effect.

The apparatus used in this new work is essentially the same as that formerly described, except that the electrode has been modified to a conical form to allow a wider beam of light to strike the metal, and to protect the glass walls from charging. A diffusion pump was used during all observations, and always maintained a pressure not measurable on a McLeod gauge. The potential on the plate was varied between -3 and -15 volts, and gave entirely parallel results over that range; for the most part, -15 volts was used. It was thought advisable to eliminate any possible effect of the plate current on the photo-electrons. The light was therefore screened between readings, and the current

* *Phil. Mag.* xiv. p. 188 (1907).

was interrupted during readings. The measurements of photo-electric current were made with a Dolezalek electrometer of sensibility 1000 divisions per volt, earthed through an india-ink resistance of 5×10^8 ohms, giving about 2×10^{-12} ampere per millimetre.

My former observations were all made on plates of cast bismuth; and it was suggested in my paper that a possible explanation of the results obtained was an orientation of the elementary crystals due to the passage of the current. This possibility was satisfactorily disposed of by making observations on plates cut from large crystals of bismuth, obtained by very slow cooling of a melt. Plates cut in various directions gave entirely comparable results. Confirmation of this conclusion was afterwards obtained from the results with films formed by evaporation, which are almost certainly non-crystalline.

The most important point requiring experimental evidence is the question of the effect of temperature. In order first to find what changes of temperature were taking place in the bismuth plate, a constantan-copper thermo-junction was soldered to the back of the plate, the flattened leads being led out through the de Khotinsky cement in the ground-glass seal. With this arrangement it was found that the temperature rise corresponding to a rise of photo-electric current of 16 per cent. was less than 5°C , and corresponding to 30 per cent. was only 24° . From these measurements alone, it seems very improbable that the observed changes of photo-electric current can be ascribed to changes due to temperature.

A few runs were made with a tungsten heating grid inserted behind the bismuth plate. This gave in every case a fall of photo-electric current, which in some cases was very considerable. The results were, however, too irregular to allow them any great weight in the interpretation of the effect.

An apparatus was next constructed to heat the bismuth plate without the use of a current. A brass tube was made to fit the ground seal of the glass apparatus, and the bismuth plate was cemented and wired to the end of this tube. A stream of water of known temperature could then be circulated to bring the plate to that temperature. The arrangement proved to be air-tight up to a temperature of about 50°C ., where the cement began to fail. Over the range from 15° to 50° , the photo-electric current remained unchanged within 2 per cent. Cooling to the neighbourhood of 0°C . lowered the sensitivity by 5 per cent.

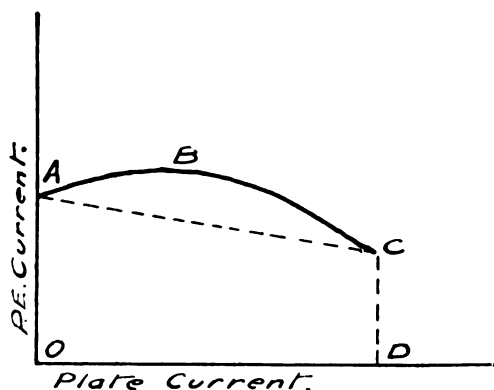
These experiments were deemed sufficient evidence that

the effect is not governed by temperature changes, but by the passage of a current through the metal giving the photo-electric emission. Further evidence of this was, moreover, obtained in the later work, which was extended to a variety of other metals; very interesting results were obtained.

Copper foil was first used, and gave results differing widely from bismuth, but much more closely reproducible. The rise of photo-electric current with increasing plate currents took place very much as with bismuth, but the maxima were attained very much more quickly. Above a certain plate current, however, the photo-electric current began to decrease, and eventually fell below its initial value. With the plate current now cut off, the electrometer readings rapidly passed through the former values, rising to the same maximum and then decreasing to the original value. This cycle could be repeated many times. Such a series of values bears a close resemblance to the curves given by Hallwachs, although in the present case the copper never reached a temperature higher than -250° . A typical curve is given in fig. 2, A.

But still more peculiar was the observation that, starting from the original value of the electrometer reading, the passage of a large plate current carried the photo-electric current directly to the lower value, and from this low value it returned to the initial value by passing through the same maximum as had before been observed.

Fig. 1.



Referring to the small diagram (fig. 1), gradually increasing plate current carries the photo-electric current over the curve A, B, C. The return with plate current cut off is by C, B, A in the course of about 1 hour. Now the

current represented by O D carries the photo-electric current directly and rapidly from A to C ; but with current cut off, the return is again by the route C, B, A. The nature of this cycle, and the fact that it is reproducible within 2 per cent., would appear very difficult to reconcile with an explanation of the phenomenon, based on changes in the gas-content of the metal.

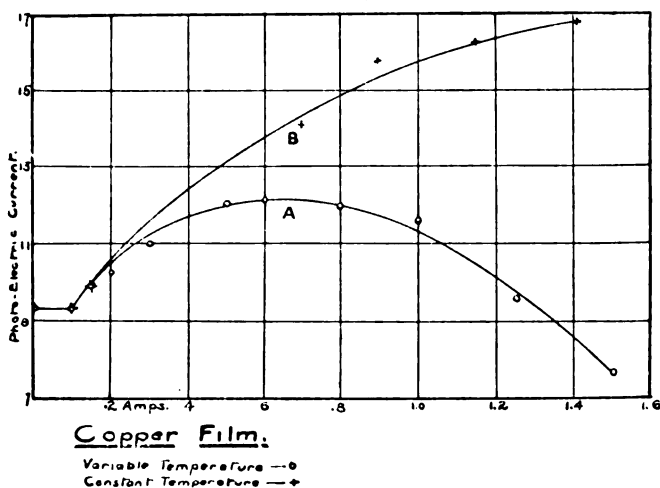
Up to this point, the work was all carried out with polished surfaces, which naturally show considerable differences. In order to eliminate such differences, it was decided to try to work with metallic films formed by evaporation from a hot electrode in a vacuum. To produce such films from electrodes of the metals themselves is a very tedious job, because of the low vapour pressure at the temperature at which it is necessary to work to avoid burning out the electrode. A very easy way of avoiding this difficulty was found. A grid was made of tungsten wire, and this was thinly electro-plated with copper. After baking at a red temperature to eliminate water and absorbed gas, the temperature was run up to just under the melting-point of copper. Thick films on glass could be formed in this way in two or three minutes. The proper temperature could be judged after very little practice. Perfect mirror films of copper were produced of resistance between $\frac{1}{2}$ and 1 ohm for dimensions of 1.2×1 cms. Nickel, gold, and silver were also successfully deposited. To plate silver on tungsten it was found necessary to first plate with nickel. Platinum it was found impossible to plate by this method in the small apparatus in use, on account of the high temperature necessary.

Copper films of this kind showed the same characteristic changes of photo-electric current as had copper foil. Fig. 2 A gives the curve obtained with a film of resistance .4 ohm. As in the case of copper foil, the film could be taken over the cycle A B C B A or A C B A, with deviations of less than 3 per cent. All the copper films gave the same characteristics.

A test of the effect was next made in which temperature changes were practically eliminated. The glass plate with its copper film was cemented to the open end of a glass tube constructed to fit the ground joint of the apparatus. The film was in its usual position close to the electrode, and could be kept at constant temperature by a stream of water against its back surface. The leads were flattened copper and were brought in through the de Khotinsky cement seal. Very striking results were obtained with this arrangement.

The photo-electric current began to increase at very nearly the same film current as before, but the increases were much more marked. Moreover, though increases as high as 70 per cent. were observed, no decrease occurred for currents which had before carried the readings well below the initial value (see fig. 2 B). A further peculiarity was observed when the current was cut off: a decrease of only a few per cent. took place, and the readings then remained constant over a long period. Standing in air or hydrogen for several days had no effect, for, on repumping, the surface showed increases of sensitivity of only 5 per cent. for currents which before produced 70 per cent. increase.

Fig. 2.



The water was next removed from the cooling tube, and current passed through the film, until the plate heated to about 40°C . After cooling and standing for some hours observations were again made. The rise of photo-electric current now made its appearance again, though only to the extent of about 25 per cent. It was apparently impossible for the plate to completely regain its original condition under these experimental conditions; but the indications were that, if heating to a considerably higher temperature were possible, the film would have returned to its first state.

From the experiments just described, it is not unnatural to conclude that the condition produced in a surface by an

electric current is permanent until a considerable rise in temperature takes place.

Of the other metals examined, gold acted in a manner very similar to copper. No attempt was made to follow its characteristic curve closely, but sufficient observations were made to ascertain that it showed a maximum followed by a decrease to well below the initial value. From this low value, however, it returned to the initial value directly, thus differing from copper.

Films of nickel and silver showed characteristics similar to bismuth, but silver proved to be much more rapid in its changes of sensitivity. Nickel showed increases of as much as 50 per cent., but was rather irregular in the return with no current passing. Neither nickel nor silver showed the fall in sensitivity observed in gold and copper for large currents.

As before stated, films of platinum could not be produced in the depositing apparatus used: and, therefore, foil had to be made use of. An attempt was first made to reproduce Ladenburg's observation that successive heatings and coolings of platinum by means of a current finally produces constant photo-electric sensitivity independent of temperature. This effect could not be detected at all for the small temperature variations obtainable in the apparatus in use, the value of the photo-electric current for any plate current being very closely the same after many heatings.

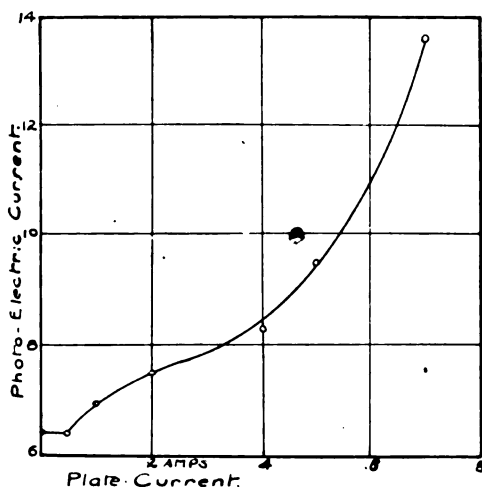
The curve of a run on platinum foil for currents up to 7 amperes is given in fig. 3. It will be observed that the increases are very large, though the temperature could not have risen above 200° C. This statement can be made because of the fact that the soldered connexions of the foil did not fail even with a plate current of 12 amperes. Observations of photo-electric current could not be made above 7 amperes plate current, because above that point the expansion of the leads allowed the foil to touch the electrode.

An attempt was made to discover some co-ordination between the changes of photo-electric effect and contact-difference of potential. Very small changes of contact-potential occurred, which showed no parallelism with the photo-electric changes, possibly due to the fact that air had to be allowed into the apparatus in order to measure the contact difference of potential.

Considering our knowledge of the amounts of gas that are absorbed by metallic surfaces, it is natural to try to base the explanation of phenomena such as have been described on

the variation of the amount and distribution of gas held by the metal. To base the explanation on changes actually produced by an electric current on the electrons and binding forces of the metal itself is very difficult, because of the semi-permanent nature of the changes observed. No theory of metallic conduction has any characteristics which could be used for this purpose. This does not, however, necessarily negative the possibility of an effect of this kind being due to current alone, because theories of conduction do not concern themselves at all with the surfaces

Fig. 3.



Platinum Foil:

of the conductors, and such boundary conditions are all-important for the photo-electric effect. The observations on bismuth warmed without the use of current, and on copper cooled while current was passing, are, I consider, very strong evidence that the effect is not produced by the heating due to the current. There is the possibility that current itself may influence the gas-content of the metal; but, considering all the evidence and particularly the peculiar cycle through which copper can be taken repeatedly and accurately, such an explanation is extremely improbable.

E. T. Whittaker, F.R.S., has recently published a new theory of the quantum mechanism* in the atom, depending on a model in which there is a circular magnetic current.

* Proc. R. S. E. vol. xlii. pt. ii. p. 129.

The quantum relation in the photo-electric effect can be easily deduced from this model. Moreover, since the magnetic current is equivalent to a charged condenser which would be turned with its plane perpendicular to an electric field of force, it is possible that this model might account for Hallwachs' observation of the decrease of photo-electric emission for large currents. But, unfortunately, it has no characteristics which would account either for the complicated changes described above or for their semi-permanent character.

I am, therefore, led into the unsatisfactory position of drawing the conclusion that the changes of photo-electric sensitivity observed must be due to changes produced in the metal by the current passed through it, without in any way being able to approach an explanation of the mechanism by which that result could be produced.

XCV. *The Resistance of a Hot Wire in an Alternating Air Current.* By R. C. RICHARDS, M.Sc. (Lond.), B.A. (Cantab.), Assistant in the Physics Department, University College, London*.

1. Introduction.

THE resistance of a hot wire in a steady direct current of air has been studied in great detail by many experimenters; and perhaps the most complete treatment of the problem is to be found in a paper of L. V. King†, to whose elegant analysis the reader is referred. The type of relation holding between the resistance and the stream-velocity is by no means simple when considered generally, and is represented graphically by curves of the type shown in fig. 1 (R-V curves). The initial portions of these curves have been studied by Tucker and Paris‡, who came to the conclusion that the drop in resistance produced by a small velocity was proportional to the square of the velocity.

This empirical relation is undoubtedly a very close one, but it must be remembered that the cooling effect of the stream for low velocities is comparable with the radiation heat losses; and therefore the Tucker and Paris relation represents the combined effect of the two cooling factors on

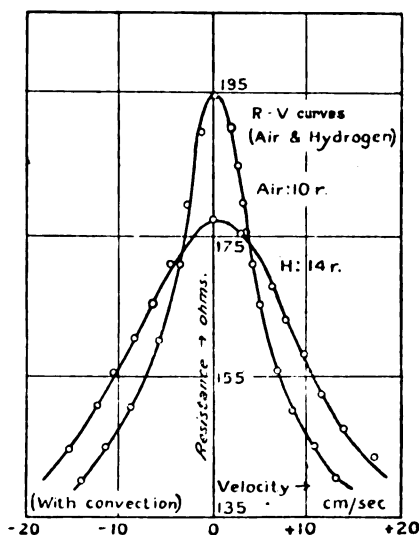
* Communicated by Prof. A. W. Porter, F.R.S.

† King, Phil. Trans. Roy. Soc. cxciv. A, p. 373 (1914).

‡ Tucker & Paris, Phil. Trans. Roy. Soc. cxxxi. A, p. 389 (1921).

the resistance of the wire. It will be noticed that the resistance reaches a minimum value beyond which an increase in stream-velocity does not further reduce it. Moreover, this minimum resistance is considerably higher than that which the wire would have if its temperature were the same as that of the stream.

Fig. 1.



If the cooling air-current, instead of being direct, were made to alternate so that the velocity at any instant is a simple harmonic function of the time, the general cooling of the wire becomes more complicated, consisting of a steady cooling effect and a superposed oscillatory effect. It is the purpose of the experiments described below to investigate these two effects in their relation to the amplitude and period of the cooling oscillatory draught.

2. Experimental Arrangements.

A standard hot-wire microphone was mounted on the prong of an electrically excited tuning-fork whose amplitude of vibration was maintained at a constant value*, and could be determined by means of a travelling microscope. As the fork was set in vibration the hot wire was thus carried to and fro in an harmonic fashion, and was

* See Note on Amplitude Control.

therefore, in effect, subjected to an harmonic draught. Great care was taken to shield the wire from extraneous draughts.

The wire was balanced electrically in the fourth arm of a Wheatstone net, by which its resistance could be determined. The net was so arranged that the wire was supplied with a constant heating current. Either of two galvanometers could be used, a d'Arsonval or an Einthoven string galvanometer, as the instrument indicating the balance of the Wheatstone net, the former for obtaining the steady drop in resistance and the latter for the oscillatory component. By moving the hot wire along the prong of the fork, it could be made to swing through the different amplitudes, which could be calculated in terms of the end amplitude of the prong and the distance from the end of the fork*.

Sets of readings were taken with various forks of the amplitude of swing of the hot wire and the corresponding steady resistance drop and amplitude of the oscillatory component. This latter was taken to be proportional to the amplitude of swing of the Einthoven galvanometer hair, whose shadow was highly magnified by an optical projector. In all observations on the oscillatory change the steady resistance was first "balanced out" and the galvanometer hair adjusted "out of tune" by the tensioning arrangements.

For very low frequencies—of the order of 1 or 2—the hot wire was caused to vibrate on the end of a long metal rod oscillating under the influence of gravity, like a pendulum.

3. The Observed Effects.

It is convenient to classify the various draughts with respect to their frequencies into three groups: (a) low-frequency draughts (2 or 3 per second); (b) medium frequency draughts (50–60 per sec.); (c) high-frequency draughts (120 and over, per sec.), and to deal with the two resistance changes—(α) steady drop, (β) oscillatory change—separately.

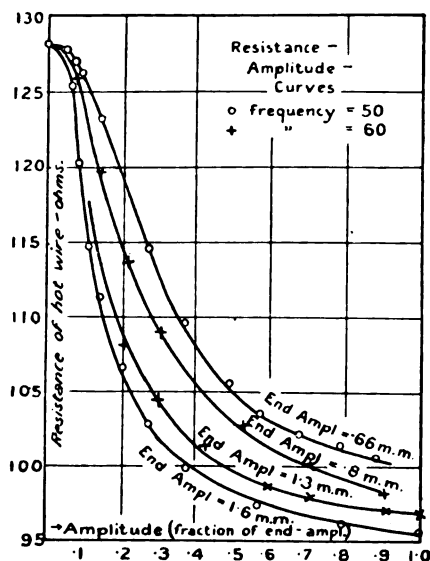
(a) The Steady Drop.

- (a) A low-frequency oscillatory draught produces no steady drop in the ordinary meaning of the term. The average resistance is lowered, but it returns to its full value twice in every vibration if the imposed draught is at right angles to the direction of the natural convection current, and once per period if the vibration is along this convection current.

* Rayleigh, 'Sound,' 1st ed. vol. i. p. 231 (1877).

- (b) A medium-frequency draught produces a steady drop in resistance which varies as the amplitude increases, as is shown by the graph (fig. 2). It is immediately apparent that this graph is very similar to the steady draught (R - V curves). Moreover, careful examination shows that the region of the curve round about the axis of the amplitude is very nearly parabolic; and thus the steady drop is proportional to the square of the amplitude and therefore to the energy in the oscillatory draught*.

Fig. 2.



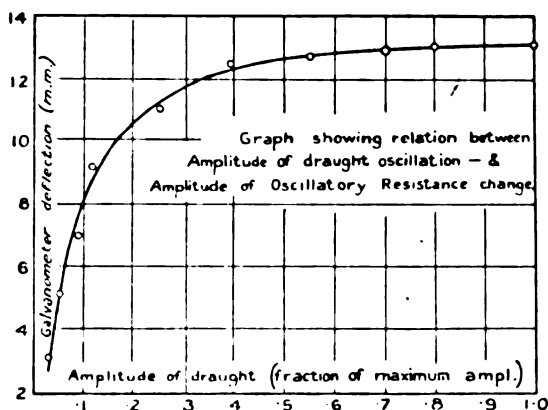
- (c) For high-frequency draughts the steady drop follows the same general lines as in (b) above. Curves of precisely the same type were obtained.
- (β) *The Oscillatory Change.*

- (a) The change is almost completely oscillatory. The resistance of the wire evidently keeps at the "equilibrium value" characteristic of the velocity of the draught at any instant. The change in frequency, due to swinging the hot wire in a vertical direction, is brought about by its swinging upwards in its own warm convection current. We thus have cooling on the down journey and recovery on the up.

* Cf. Tucker & Paris, *ibid.* p. 410.

- (b) The amplitude of the oscillatory change is found gradually to increase with increasing amplitude, and to attain a maximum value independent of further increase in amplitude. This is shown in fig. 3. It is to be noted that for small values of the exciting amplitude the oscillatory change is proportional to it*. The frequency of this oscillation could be investigated by means of a telephone, replacing the galvanometer in the bridge arrangement. The note heard is the higher octave of the note given by the tuning-fork, and hence, as one would expect, the frequency is twice that of the exciting vibration.

Fig. 3.



- (c) For high-frequency draughts the oscillatory change becomes very small. It can be detected in a telephone, but it was quite impossible to measure its amplitude by means of the string galvanometer.

4. Theory of the Effects.

We may arrive at a tentative explanation of the above effects by imagining that the resistance of the hot wire will always "follow" (*i.e.*, will always assume the equilibrium value corresponding to) an *increasing* velocity; but its recovery depends upon the rate at which it can draw energy from the external source of current. This is equivalent to saying that the draught can cool the wire down—at the expense of its temperature,—but cannot warm it up again.

Let R be the resistance of the hot wire in still air, it being

* Cf. Tucker & Paris, *ibid.* p. 410.

heated by a current produced by a voltage E . Suppose that a current of air be passed over it, reducing its resistance to R ohms, and the draught suddenly cut off.

At the moment of shutting off the draught, the rate of supply of heat is

$$= \frac{dH}{dt} = \frac{E^2}{4 \cdot 2R} \text{ cal./sec.}$$

If the supply of dH calories to the wire raises the temperature $d\theta^\circ \text{C.}$,

$$dH = msd\theta$$

(m = mass of wire, s = specific heat of wire),

but

$$\theta = \text{temperature of the wire} = \frac{R - R_0}{R_0 \alpha}$$

(R_0 = resistance of wire at stream temperature, α = temperature coefficient of resistance);

$$\therefore d\theta = dR/R_0 \alpha.$$

So we have

$$\frac{ms}{dt} \times \frac{dR}{R_0 \alpha} = \frac{E^2}{4 \cdot 2R}$$

or

$$RdR = \frac{E^2 R_0 \alpha}{4 \cdot 2ms} dt;$$

and if the resistance rises from R to R' in a time t , we have

$$\int_R^{R'} R dR = \frac{E^2 R_0 \alpha}{4 \cdot 2ms} \int_{t=0}^{t=t} dt;$$

$$i. e., \quad R'^2 - R^2 = \frac{E^2 R_0 \alpha}{2 \cdot 1ms} t. \quad \dots \dots (1)$$

If the amount of resistance recovery, *i. e.* $R' - R$, is small compared with R ,

$$R' - R = \frac{E^2 R_0 \alpha}{4 \cdot 2msR} t. \quad \dots \dots (2)$$

The wire being acted on by a draught whose period is T , the wire will have a time $T/4$ for recovery. If R is the resistance of the wire corresponding to $v=0$, the actual time for total recovery would be given by

$$\bar{R} - R = \frac{E^2 R_0 \alpha}{4 \cdot 2msR} \cdot t = \frac{A}{R} t \quad (A = \text{a constant}) \quad \dots (3)$$

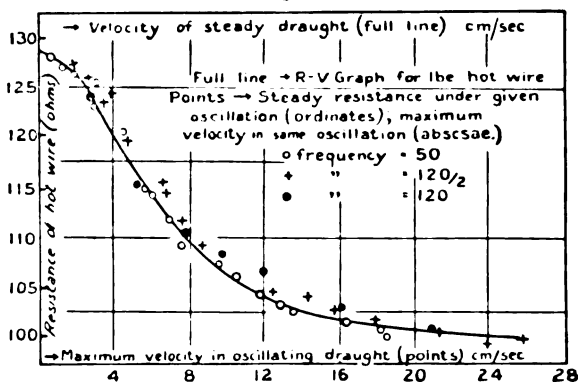
Now if $T/4$ is equal to t or greater than t as given above, R being the resistance corresponding to the maximum resistance in the draught, the wire will completely recover its resistance twice every period.

If $T/4$ is $< t$, the resistance will not recover completely, and a steady drop effect will be produced.

Of course, in practice the time for recovery will be greater than that given by (3), because the wire is not recovering unhindered, as we have assumed, but is still subjected to the decreasing draught in the oscillation. This point must be kept in mind when we come to test the theory quantitatively.

The similarity between the R - V curves (fig. 1) and the Resistance-Amplitude curves (fig. 2) leads one to suspect that the total (steady) resistance drop is one which would be produced by a steady draught proportional to the amplitude of the oscillation for a given frequency, or for any frequency and amplitude proportional to the maximum velocity in the oscillating draught. That the main part of the steady drop in resistance is accounted for in this way is clear from the graph below (fig. 4). The full line is the

Fig 4.



R - V curve for the wire under experiment. The other points are derived from the amplitude-resistance readings for the 50, 60, and 120 forks. The abscissæ are the maximum velocities in the oscillating draught, and the ordinates the resistances corresponding to that amplitude from which this maximum velocity has been derived.

It appears, therefore, that the resistance assumed by the hot wire is very nearly the equilibrium resistance corresponding to the maximum velocity in the oscillating draught.

Since this velocity is given by $2\pi na$ (n =frequency, a =amplitude), it follows that, provided $n \times a$ is constant, the steady drop would be the same for oscillations of different frequencies. This is shown in fig. 4. The points for the 50, 60, and 120 forks lie very nearly on the same curve.

Referring to equation (3), it will be seen that the amplitude of the oscillatory change is inversely proportional to R , the lowest resistance produced by the draught, for a given value of T , the period of the imposed oscillation. Plotting this amplitude against $1/R$, the reciprocal of the lowest resistance produced by the draught does not give a straight line, but a curve which degenerates into a straight line for very large values of $1/R$. As has before been pointed out, we cannot expect that equation (3) will do more than generally indicate the relations we find, and this it does satisfactorily. For example, the amplitude of the oscillatory change was seen (fig. 3) to increase with the amplitude of the exciting vibration, and to reach a constant maximum value. Now, as this draught amplitude increases, R , the lowest resistance, decreases (fig. 2), and reaches a constant minimum value: the relation between the amplitude of the oscillatory change and that of the imposed draught is therefore seen to be, in general, in agreement with the simple theory.

Again, fig. 3 shows that the oscillatory change is, *ceteris paribus*, inversely as the frequency. This explains why, for two frequencies, this change is large, and why it practically disappears for high frequencies.

5. Note on Amplitude Control.

A hot wire attached to the prong of a tuning-fork provides a very sensitive amplitude indicator. Referring to fig. 2, if the hot wire be adjusted to work on the region of the curve which is nearly vertical (AB), a small alteration in amplitude will produce a large change in its resistance. The wire being balanced in a Wheatstone net and oscillating at a desired amplitude, will immediately throw the bridge out of balance if the amplitude changes. Steps can then be taken to restore the original amplitude, which will be restored when the bridge indicates balance once more. The writer found that this method would detect a variation in amplitude not observable in a microscope mounted over the vibrating tuning-fork.

6. Summary.

The two resistance changes produced by an alternating air current in a hot wire are examined separately and found to follow, at least approximately, some simple relations. An

elementary "recovery" theory is described, which the writer thinks may be capable of elaboration.

It is hoped that the work may be useful in connexion with the applications of the Tucker hot-wire microphone, as indicating a method of making the instrument sensitive to higher frequencies than has yet been found possible.

The writer's acknowledgements are due to Sir J. J. Thomson, O.M., under whose guidance this work was carried out; and to Dr. Tucker and Mr. Paris for an illuminating discussion on the subject in the summer of 1921.

Physics Laboratory,
University College, London.
February 1923.

XCV. *The Mass-spectra of Chemical Elements.*—Part IV.
By F. W. ASTON, D.Sc., F.R.S., Fellow of Trinity College,
Cambridge*.

[Plate XIII.]

IN several previous papers† an account of the mass-spectrograph has been given, and the results of analyses carried out by its means described. The following communication deals with similar work continued up to the end of 1922. As already pointed out the work becomes increasingly difficult as the elements under study become less and less suitable for use by standard methods. Many attempts have consequently proved abortive. It is proposed, however, to give some account of both failures and successes, for the results of the former, though negative, often raise points of great interest. As in the previous papers the description of the experiments follows, as far as possible, the order of the experiments themselves.

The general technique has been much the same as that used before except that in most of the more recent work the discharge-tube has been run much "softer." 20 to 30 kilovolt rays are used and the current pushed up to two or more milliamperes. This lessens the risk of coil breakdown and brings the magnetic deflexion of the heaviest elements within the working-range of the existing apparatus. The most important advance has been made quite recently in connexion with the photographic plates employed.

* Communicated by the Author.

† Phil. Mag. xxxix. p. 611; xl. p. 628; xlii. p. 140; xlii. p. 436.

Schumannised Plates.

The action of positive rays on photographic plates, unlike that of light, is purely a surface effect, so that great improvements are to be expected if the concentration of the sensitive grains on the surface is increased. Experiments in this direction have already resulted in very marked success, and it is hoped to give a detailed account of these as soon as a method which gives satisfactory uniformity has been worked out. It will be enough here to state that the process, to which the term "Schumannising" may be applied, consists in partially dissolving the gelatine emulsion away from the plate by means of dilute sulphuric acid. The object is not to remove the gelatine as far as possible, as in the ordinary Schumann plate, but to obtain high surface concentration without making the plate too difficult to handle in the ordinary way. The writer is much indebted to Professor T. R. Merton for information on this very valuable device.

Experiments with Helium.

At the request of Professor McLennan, samples of helium from the Canadian gas-wells were subjected to analysis and carefully examined for the presence of isotopes or other abnormalities. None were observed. This opportunity was taken to endeavour to obtain evidence of the presence of doubly charged helium atoms He^{++} . The alpha rays consist of such particles, and since the potential necessary for the double ionization is of the order 80 volts they must certainly occur in the positive ray discharge-bulb. The importance in the present instance is that the second order line of helium, apparent mass 2.00(0), if obtained on the mass-spectrum would be just separated from the hydrogen molecule line 2.01(5) on the present instrument, and would give an exceedingly accurate and reliable measure of the relative masses of the two bodies. Many plates were taken under a great variety of conditions, but in no case could a line be detected in the expected position near the H_2 line. The most probable explanation seems to be that the sphere of action of a particle with an ionization potential of 80 volts is so large that a negligible percentage, if any, of the doubly charged helium nuclei are able to pass the slit system and the analysing fields without collision with, and capture of, a stray electron.

NICKEL (At. Wt. 58.68).

The obvious compound to use in investigating this element was Nickel Carbonyl. In the earlier experiments of Sir J. J. Thomson with this substance it had been found exceedingly troublesome to deal with. On entering the discharge-tube it immediately decomposed, and the metal deposited on the walls as a black mirror soon prevented normal discharge altogether. In the present experiments this difficulty was overcome to a sufficient degree by diluting the vapour of the carbonyl with CO_2 and running the maximum safe current through the tube to lessen the necessary exposure. The mass-spectra obtained, though not strong enough for reproduction, were quite easy to interpret and showed conclusively that nickel consists of two isotopes 58 and 60. The intensity relation between their lines agrees well enough with the mean atomic weight quoted and supplies a simple explanation of the long discussed anomaly of the atomic weights of nickel and cobalt. The two nickel lines when measured against mercury lines of the third and fourth order as standards show no measurable deviation from the whole number rule.

Experiments with Metallic Chlorides.

In the cases of many out of the large number of elements yet to be analysed the only stable and easily obtainable compounds with a reasonable vapour pressure are chlorides. This is unfortunate in many ways. In the first place most of these chlorides have a violent action on rubber tap grease. In the present form of apparatus the vapour has to pass several stopcocks and it is quite possible that the most active ones are entirely decomposed and never reach the discharge at all. Even if this difficulty were removed by alteration of the admission arrangements there still remains a more serious one. This is that the passage of the discharge in such compounds must inevitably release free chlorine. The latter can, and apparently does, form volatile compounds with practically every element used in the construction of the apparatus, including the aluminium of the electrodes and the silicon of the glass. The result is a perfect maze of lines filling every successive unit place and effectually screening any clear vision of the lines of the element under observation. This effect is enormously exaggerated by the proclivity of chlorine to form hydrogen addition products, and also by its isotopic constitution since for every type of combining particle there will be two lines due to the monochloride, three to the dichloride, four to the trichloride, etc.

Thus titanium chloride gave spectra of great complexity but perfectly useless for identifying the isotopes of the metal, even if their lines were present, since all the units from 44 to 52 were filled by lines of various intensities. There was a group of lines 82-86, the last four of which were very strong. Now titanium has an atomic weight 48.1, so one might easily have been led to the identification of these as its monochlorides and hydrochlorides. Fortunately, however, this characteristic group had been obtained before with tin tetrachloride, a compound of similar chemical properties. It is probably due in the main to CCl_2 and CHCl_2 derived from the action of the metallic chloride on the tap grease. If the reader will refer back to plate vii., *Phil. Mag.* vol. xlii. the group will be seen plainly near the strong Hg band on Spectrum II.

Chromyl chloride was even more hopeless for its action on tap grease and wax was so rapid as to make it quite unworkable.

Experiments with Lead Ethide and Zinc Methide.

When the apparatus had been thoroughly cleaned from the effects of the chlorine compounds an attempt was made to obtain the lines of lead by the use of its volatile tetraethide. The writer is indebted to Sir W. Pope for a sample of this compound and also for the titanium chloride already mentioned. The importance of settling the much discussed isotopic constitution of ordinary lead is obvious, but unfortunately the experiments gave no results of any value. No signs of lines were visible in the expected region although very long exposures were resorted to. If, as is possible, this negative result was caused by the abundant liberation of carbon and hydrogen compounds from the decomposing ethide, the difficulty might be reduced by the use of the simpler methide. The experiments will be repeated when this compound is available, but hope of success in this direction has been already discounted by some later experiments with zinc methide which failed entirely to give the zinc lines. The values of the latter are already known from the fine work of Dempster* but confirmation by the mass-spectrograph would have value, particularly in connexion with the accuracy of the whole number rule.

On introducing the vapour of zinc methide into the discharge-tube only one new line made its appearance. This

* A. J. Dempster, *Phys. Rev.* xx. no. 6, Dec. 1922.

one was quite obvious and at a point corresponding to mass 127. It is doubtless due to the presence of traces of iodine derived from the methyl iodide used in the manufacture of the methide. When one considers that the sample was a perfectly colourless one and described as chemically pure, this is a striking illustration both of the selective quality and the extraordinary delicacy of analysis by positive rays.

Further Experiments with Xenon.

It has been pointed out * that whereas the atomic weight of xenon calculated from Moore's determination of its density is 130.2 †, that deduced from the results of the mass-spectrograph is about one unit higher. No great accuracy is claimed for the latter method but the discrepancy is rather larger than is to be expected and it has been suggested that the density result might be really too low owing to the possible presence of krypton as an impurity.

A welcome opportunity to put this point to the test was afforded during the recent visit to Cambridge of Dr. R. B. Moore, who kindly brought over from Washington a small sample of the original xenon which had been used for the density determination. Several mass-spectra were obtained with this gas, but although considerable exposures were given no definite evidence of the krypton group of lines could be detected. Since krypton is very sensitive to positive ray analysis this result shows that it could not possibly have been present to the extent required to account for even a small fraction of the discrepancy, which therefore remains unexplained.

These experiments had indirect results of importance, for the residual xenon in the discharge-tube gave excellent lines on some of the first experimental schumannised plates. These not only established a point of fundamental importance in connexion with the element, tin, considered below, but confirmed beyond doubt the presence of two weak xenon isotopes 128, 130 previously suspected. Owing to the completely changed characteristics of the plates these could now be clearly distinguished on the original negatives, and may be seen each side of the strong 129 line on Spectra I and II of the plate.

More recently during a search for an inert element of high atomic weight in the atmosphere, a full account of which

* F. W. Aston, 'Isotopes,' p. 114.

† H. E. Watson, Trans. Chem. Soc. p. 836 (1910); R. B. Moore, *ibid.* p. 2181 (1908).

will be published later, two new components of xenon were discovered at 124, 126. These give very faint lines only distinguishable on spectra in which the ordinary xenon lines are enormously over exposed. There is every reason to suppose that they are due to two isotopes of xenon present in exceedingly small quantities, probably less than one-tenth per cent. of the whole. The line at 126 appears slightly stronger than that at 124. As all the possible reference lines were hopelessly over-exposed these numerical values are only approximate.

TIN (At. Wt. 118·7).

In some earlier experiments with tin tetrachloride the complex nature of the element was suspected but not conclusively proved, it has now been satisfactorily demonstrated by the use of tin tetramethide, a specimen of which was kindly supplied by Sir W. Pope. The first experiment with this substance was perhaps somewhat fortunate and the spectra obtained on this occasion present features of great interest. Some of them are reproduced on the plate, Spectra I, II, and III. Spectrum I was taken before the tin compound was introduced. Its principal lines are those of xenon residual from the previous experiment and mercury. Spectra II and III show the new lines due to tin and its compounds. The element is evidently highly complex, it has isotopes 116, 117, 118, 119, 120, 122, 124 and a faint possible eighth at 121. The order of intensity can be seen on the plate and is given in the table at the end of the paper. The intensities are such as to preclude the possibility of any of the lines, except the very faint one at 121, being ascribed to hydrogen addition products. Satisfactory confirmation of the isotopic nature of the lines is provided by the reproduction of the entire complex group with identical intensity relations, 15, 30 and 45 units higher up the mass-scale, due obviously enough to SnCH_3 , $\text{Sn}(\text{CH}_2)_2$, and $\text{Sn}(\text{CH}_3)_3$. A reference to the mass-spectrum obtained with tin tetrachloride and reproduced in the plate already mentioned*, shows that the tin lines were really obtained then, but the disclosure of the fainter components lying between pairs of stronger ones has only now been made possible by the remarkable improvement in definition given by the new type of plate.

Measurements of the lines of tin show that while their masses are integral within experimental error with regard to

* Plate vii. Phil. Mag. vol. xlii.

each other, yet when compared with the other lines on the plate they give values *less than whole numbers by 2 to 3 parts in 1000*. This remarkable result would certainly have been suspected of being an experimental error had it not been for the fortunate presence of the xenon lines on the plate, and the appearance of the lines of tin monomethide amongst them. There are two strong xenon lines at 134, 136 which have been compared with the lines of mercury in previous experiments, and there is no reason to doubt that they are integral to about 1 in 1000. The strongest tin monomethide line $\text{Sn}^{120}(\text{H}_3)$ should lie evenly between these two lines. It is very clear that it does not do so, but, on the contrary, is shifted so far to the left as to coalesce partially with Xe^{134} so that the latter appears broadened. This marked asymmetry is repeated in another part of the plate in Spectrum III taken with a stronger magnetic field.

It seems impossible to imagine any instrumental defect which could give rise to this shift. There appears, therefore, to be no escape from the conclusion that tin and xenon cannot both obey the whole number rule. It was realized and emphasized* that this rule was not to be expected to hold with mathematical exactness owing to the packing effect, but it is very surprising that elements only differing by three units in atomic number should show so large a divergence. It seems probable that the divergence from the mean ($O=16$) is greater in the case of tin than in that of xenon, but since the arithmetic sum of the two (supposing them to be of opposite signs) is only about three times the experimental error, satisfactory settlement of this point will have to be deferred till an instrument of higher precision is available.

IRON (At. Wt. 55.84).

This element was investigated by means of its volatile carbonyl. A sample of this somewhat rare compound was obtained from the Chemical Department through the kindness of Mr. W. H. Mills. The experimental treatment was the same as that described above for the nickel compound, but the difficulties were more pronounced and the results not so definite. One of the spectra obtained is reproduced, Spectrum IV on the plate. The only line which can be ascribed with certainty to iron is the one at 56. The faint line at 54 may possibly be an isotope, but this is by no means certain. Thirteen independent measurements of the principal line relative to other lines on the plate gave values

* Phil. Mag. xxxix. p. 624.

of its mass which were very consistent and had a mean of 55.94. This only differs from the chemical value by 2 in 1000 so that it is by no means unlikely that iron is a simple element.

Experiments with Cadmium and Thallium.

The boiling point of cadmium, 778°C ., is not excessively high so it was hoped that its mass-spectrum would be obtained if the metal was volatilized inside the discharge-tube. The method adopted for carrying this out was to lower a quartz glass vessel containing a small quantity of the substance into the path of the cathode ray beam by means of a winch. By careful adjustment of the position of the vessel it could be raised to any desired temperature up to a bright red heat. The cadmium was vaporized without the least difficulty and immediately condensed as a bright mirror on the cooler walls of the tube, but the vapour pressure could not have been high enough to affect the discharge for the optical spectrum showed no cadmium arc lines. The mass-spectra obtained showed no signs of lines in the expected region so the experiment failed to achieve its object.

It is interesting to note that mercury was completely eliminated from the discharge almost instantaneously when the cadmium volatilized. Its lines vanished entirely from the mass-spectra and did not reappear so long as the cadmium mirror remained on the walls of the discharge-tube. This method of eliminating every trace of mercury may be of considerable value in the future. In the present instance advantage was taken of it to attempt the analysis of thallium. This element has an atomic weight of 204 so that its lines would certainly be obscured by those of mercury except under these special conditions. Thallium chloride, which is fairly volatile, was therefore introduced and volatilized, but although the lines of chlorine appeared there was no sign of any that might be due to thallium. It is possible that the cadmium layer removes the vapour of the element as effectively as it does that of mercury.

SELENIUM (At. Wt. 79.2).

Previous experiments with selenium hydride * had been completely unsuccessful, but on volatilizing the element itself by the method described above conclusive results were immediately obtained. Spectrum V on the plate shows that selenium is characterized by five strong lines 76, 77, 78, 80, 82 and a very faint sixth at 74. The true isotopic nature of

* Phil. Mag. xlii. p. 140.

this group is beautifully brought out by its repetition at a position 12 units higher on the mass-scale due to CSe and 28 units higher due to COSe . Some of the faint lines of the complex group CSe_2 may also be distinguished on the right. The evidence of the isotopic constitution of selenium is therefore exceptionally definite and satisfactory. The order of intensity of the lines can be seen on the spectrum and is given in the table; it agrees reasonably well with the chemical atomic weight. It will be noticed that no fewer than three of the isotopes of selenium 78, 80, 82 are isobaric with those of krypton.

Experiments with Tellurium and Beryllium.

The success with selenium raised hopes for tellurium which had also been attacked previously without result*. Pure tellurium element was volatilized but no lines attributable to it could be seen on the mass-spectrum. This failure is probably due to its high boiling point and consequent low vapour pressure. A second attempt was made using the more volatile tellurium chloride, but again, though chlorine was present in abundance, there was a complete failure to obtain the lines of tellurium.

Beryllium acetate was introduced, but its volatilization was accompanied by immediate decomposition and a deposit of white oxide appeared. No evidence of the line of beryllium could be seen at the expected position 9. G. P. Thomson's positive ray observations, however†, and the latest value 9.018 obtained for its atomic weight‡ leave little doubt as to its simple constitution.

ALUMINIUM (At. Wt. 26.96).

Aluminium has long been suspected of being a simple element on account of the closeness of its chemical atomic weight to an integer. This view is further supported by the rule, now known to be obeyed in so many cases, that elements of odd atomic number have few isotopes, never more than two, and that these isotopes have odd atomic weights. The occasional appearance of a faint line at 13.5 on mass-spectra taken when chlorine was present in the discharge has been ascribed to Al^{++} derived from the electrodes§.

During the experiments on tellurium chloride the chlorine liberated attacked the electrodes to an unmistakable extent. In fact the slit in use was ruined by the corrosion. It is therefore perfectly certain that volatile aluminium chloride

* *Loc. cit.*

† G. P. Thomson, *Phil. Mag.* xlii. p. 857.

‡ Horigschmid and Breckenbach, *Ber.* lv. B, pp. 4-12 (1922).

§ *Phil. Mag.* xl. p. 633.

must have been present in considerable quantity during the exposures. The indication of its presence was equally strong on the mass-spectra obtained. The line at 27, usually very much weaker than that at 28, was very intense and its second order line easily visible at 13·5. Furthermore, strong groups of lines appeared with their first units at 62 and 97. The intensities of the lines in these groups show that they are due to the mono- and dichlorides of bodies having masses 27 and 28. The latter may be an atom of Si^{28} or a molecule of CO but the only feasible origin of the former is an atom of aluminium. It is therefore reasonably certain that this element consists mainly of atoms of mass 27, and since there is no evidence of atoms of lighter mass the chemical atomic weight leads definitely to the conclusion that it is simple. Measurements of the line 13·5 show no measurable deviation from the whole number rule.

Some valuable evidence on the constitution of chlorine was obtained from these experiments at the same time. One of the spectra showed the lines 35, 36, 37, 38 exceedingly intense, with no vestige of a line at 39. It is therefore certain that the hypothetical isotope 39 does not exist in any appreciable quantity.

ANTIMONY (At. Wt. 120·2 (?)).

The failure to obtain the spectrum of antimony from its hydride has already been described*. In connexion with the successful analysis now achieved the writer wishes to record his most hearty thanks to Professor G. T. Morgan, who prepared a sample of antimony methide specially for the purpose and also supplied the samples of tellurium chloride and beryllium acetate used in the experiments just described. The antimony methide vapour was introduced mixed with CO_2 and gave exceedingly good results at once. One of the spectra obtained is reproduced in Spectrum VI on the plate. The element is characterized by two strong lines 121, 123, the former being slightly the more intense. When sufficient exposure is given similar pairs appear 15 and 30 units higher on the mass scale (*cf.* Tin, p. 939) due to the mono- and dimethide respectively. Faint companions have been seen also at 122, 124, but from their irregular intensity relations it is practically certain that these are due to hydrides. These results show that antimony is a complex element consisting of two isotopes, 121 and 123. Measurement of the lines shows no appreciable deviation from the whole number rule so that it is quite certain that the international atomic weight quoted above is much too

* Phil. Mag. xlii. p. 141.

low. On the other hand the value 121.77 recently obtained by Willard and McAlpine* is in agreement with the results of the mass-spectrograph.

Table of Isotopes and the Whole Number Rule.

So long as only one element, hydrogen, showed measurable deviation from the whole number rule it was reasonable to identify the whole numbers with the true masses of the isotopes on the oxygen scale. Now that further exceptions have been discovered—tin, and probably iron—this identification cannot be continued. No useful purpose will be served by introducing the fractional values until these can be obtained with much greater accuracy. In the following table they are omitted and the *nearest* integer given. These

Table of Elements and Isotopes.

Element.	Atomic Number.	Atomic Weight.	Minimum number of Isotopes.	Mass-numbers of Isotopes in order of intensity.
H	1	1.008	1	1
He	2	3.99	1	4
Li	3	6.94	2	7, 6
Be	4	9.0	1	9
B	5	10.9	2	11, 10
C	6	12.00	1	12
N	7	14.01	1	14
O	8	16.00	1	16
F	9	19.00	1	19
N	10	20.20	2	20, 22
Na	11	23.00	1	23
Mg	12	24.32	3	24, 25, 26
Al	13	26.96	1	27
Si	14	28.3	2	28, 29, (30)
P	15	31.04	1	31
S	16	32.06	1	32
Cl	17	35.46	2	35, 37
A	18	39.88	2	40, 36
K	19	39.10	2	39, 41
Ca	20	40.07	2	40, 44
Fe	26	55.84	(1)	56, (54)?
Ni	28	58.68	2	58, 60
Zn	30	65.37	4	64, 66, 68, 70
As	33	74.96	1	75
Se	34	79.2	6	80, 78, 76, 82, 77, 74
Br	35	79.92	2	79, 81
Kr	36	82.92	6	84, 86, 82, 83, 80, 78
Rb	37	85.45	2	85, 87
Sn	50	118.7	7 (8)	120, 118, 116, 124, 119, 117, 122, (121)
Sb	51	121.77	2	121, 123
I	53	126.92	1	127
X	54	130.2	7 (9)	129, 132, 131, 134, 136, 128, 130, (126), (124)
Cs	55	132.81	1	133
Hg	80	200.6	(6)	(197-200), 202, 204

(Numbers in brackets are provisional only.)

* Willard and McAlpine, Jour. Am. Chem. Soc. xliii. p. 1085 (1921).

integers are provisionally called "mass-numbers." The mass-number may be taken to represent the number of protons in the atom for it seems exceedingly unlikely that the packing effect will ever throw the mass out as much as half a unit. At the same time such a possibility must not be entirely ignored. The table gives a complete list of all those elements whose isotopes have been determined by any of the positive ray methods up to the present.

In conclusion the writer wishes to repeat his acknowledgement to the Government Grant Committee of the Royal Society for part of the apparatus employed in this research.

Summary.

Further experiments with the mass-spectrograph are described by which the constitution of six more elements Ni, Sn, Fe, Se, Al, Sb has been determined.

Two new isotopes of xenon have been discovered and evidence obtained excluding 39 from the isotopes of chlorine.

Deviations from the whole number rule have been observed in the case of the masses of the isotopes of tin compared with those of xenon.

A complete table is given of the isotopes of the thirty-four elements whose constitution has so far been determined by the methods of positive rays.

Cavendish Laboratory,
Cambridge, Feb. 1923.

XCVI. *The Hot-Wire Inclinometer: its Sensitivity in Air and in Carbon Dioxide.* By J. S. G. THOMAS, D.Sc. (Lond. and Wales), A.R.C.Sc., A.I.C., Senior Physicist, South Metropolitan Gas Company, London*.

Introduction.

A form of hot-wire inclinometer comprising a pair of fine heated platinum wires arranged parallel and close to one another within an enclosure has been recently described by the author†. The wires constitute two arms of a Wheatstone bridge, and the deflexions of the galvanometer depend upon the variation of the thermal conditions of the respective wires as the plane of the wires is rotated about a

* Communicated by the Author.

† Proc. Physical Soc. vol. xxxii. p. 291 (1920).

horizontal axis, either in, or at right angles to their plane. The dependence of the sensitivity of the inclinometer upon the distance separating the wires was discussed in a subsequent paper*. Humphrey† showed that the sensitivity was increased when the air surrounding the wires was replaced by carbon dioxide. Previous experience with fine heated platinum wires surrounded by various gases, made it appear improbable that this conclusion could be correct under all conditions, and the present investigation was undertaken to ascertain the criteria for greater sensitivity in one or other of the two media, air and carbon dioxide.

Experimental Results and Discussion.

Two series of experiments were carried out. In either series the inclinometer was composed of two fine heated platinum wires of diameter 0.10 mm. Particulars of the

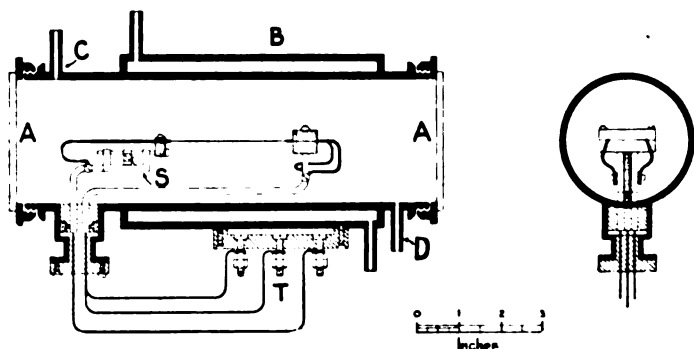


Fig. 1.

preparation of the wires prior to use have been given in the papers already referred to. In the first series, the wires were mounted in a large brass cylindrical chamber, 25 cm. in length and 7.6 cm. in diameter, the ends being closed by glass plates, A, as shown in fig. 1. In the second series the enclosure was a narrow brass tube of the same length, but only 6 mm. in diameter. Wider chambers were provided at the end of this tube for the purpose of mounting the wire. In each case the enclosure was provided, as shown in fig. 1, with a jacket B, through which tempered water maintained

* Phil. Mag. vol. xlii. p. 940 (1921).

† Proc. Physical Soc. vol. xxxiii. p. 190 (1920-1921).

throughout at $15^{\circ}\text{C.} \pm 0.5$ flowed. The bridge arrangement and the galvanometer sensitivity remained throughout the same. The wires were mounted parallel to one another at a distance apart equal to about 1.5 mm., and when heated were maintained just taut by the spring device S as described in a previous communication*. The ends of the wires were connected to terminals shown at T. The various points were made tight by means of sealing-wax, and the enclosure could be filled with either air or carbon dioxide as desired, through the tube C. D served as outlet, and was connected to a water-pump for the purpose of exhausting the chamber. Both inlet and outlet tubes were provided with taps and calcium chloride tubes for maintaining a dry atmosphere within the chamber. The chamber was mounted so as to be capable of rotation about a horizontal axis parallel to the plane of the wires, the rotation being indicated on a divided circle, and the pressure within the chamber was indicated by means of a mercury manometer.

Particulars of the wires are set out herewith:—

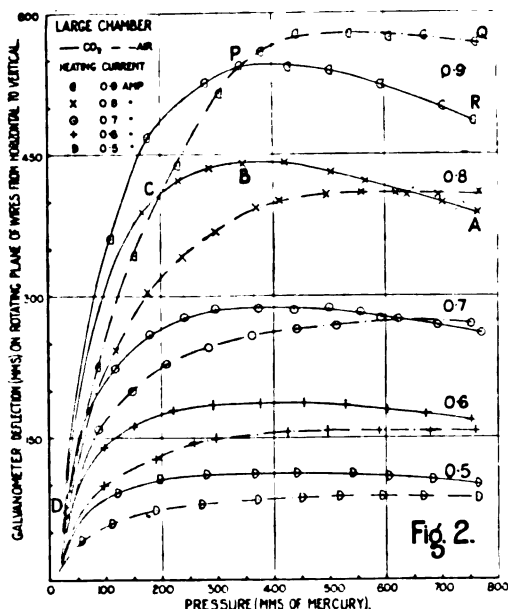
Length of each wire	7.0 cm.
Distance apart of wires	1.5 mm.
Temperature coefficient of wires	0.003226.
Resistance of each wire at 15°C.	0.934 ± 0.003 ohm.

With the plane of the wires horizontal and the bridge-current flowing through the wires in series, the bridge was balanced, the fixed arm of the bridge being throughout maintained at 1000 ohms. The galvanometer deflexion was then determined on rotating the plane of the wires from the horizontal to the vertical position, the current in the bridge being adjusted to its previous value.

The results obtained with the large chamber, when using different bridge-currents, and for various values of the pressure in the chamber are shown in fig. 2. The currents corresponding to the various pairs of curves were, 0.5, 0.6, 0.7, 0.8, and 0.9 amp. respectively. It will be observed that at atmospheric pressure (760 mm.), for equal values of the bridge current, there is a relatively small difference in the deflexion for 90° rotation, according as the medium surrounding the wires is air or carbon dioxide. Moreover, while for the lower values of the heating current, the sensitivity of the inclinometer is somewhat greater in the case of carbon dioxide, the ratio of the respective sensitivities (CO_2/Air) is very much less than that to be anticipated from

* Phil. Mag. vol. xliii. p. 278 (1922).

Humphrey's experiments*. With increase in the value of the heating current, at atmospheric pressure, the deflexion on rotation of the plane of the wires from the horizontal to the vertical becomes greater for air than for carbon dioxide, as shown by curves corresponding to currents of 0.7, 0.8, and 0.9 amp. The relative order of magnitude of the respective sensitivities is thus inverted with increase in the heating current. Attention may here be directed to two other outstanding features of the curves shown. In the case of air, with decrease of pressure in the chamber from atmospheric,

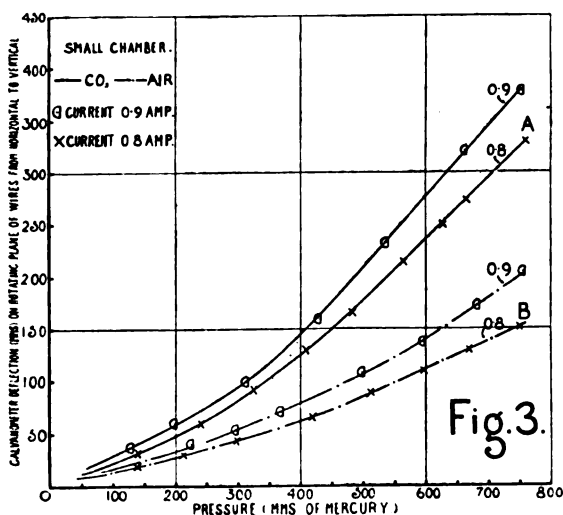


there is initially very little, if any increase of galvanometer deflexion. With carbon dioxide on the other hand, the initial decrease of pressure is in all cases accompanied by a very marked increase of galvanometer deflexion as shown, *e.g.*, by the points A and B for the curve corresponding to 0.8 amp. Compared with the ultimate very rapid decrease of deflexion accompanying a decrease of pressure, such increases are, however, comparatively small in all cases (*see, e.g.*, portion CD of curve just referred to). It will be observed that for all the respective values of the bridge

* *Loc. cit.* p. 191.

current, provided the pressure in the chamber is sufficiently reduced, the sensitivity of the inclinometer in carbon dioxide is somewhat greater than that in air and the ratio of the respective deflexions increases as the pressure is reduced.

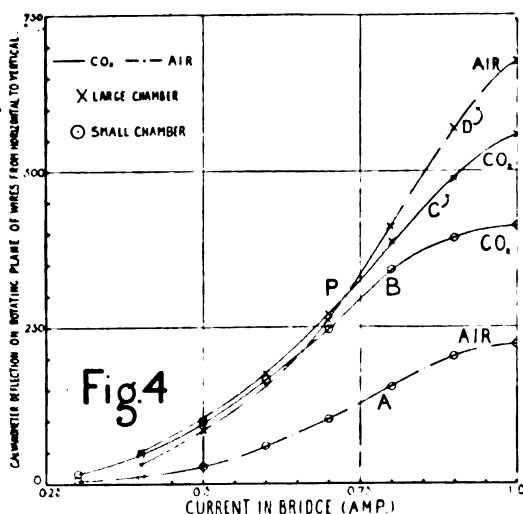
Representative curves in which the galvanometer deflexions on rotation of the plane of the wires from the horizontal to the vertical in either air or carbon dioxide respectively are plotted as ordinates against the corresponding pressures in the chamber as abscissæ, are given for the narrow chamber of diameter 6 mm. in fig. 3. Currents of 0.8 and 0.9 were employed in the curves shown. The curves differ in character



very considerably from those shown in fig. 2. Thus, for example, for a current of 0.8 amp. and a pressure of 760 mm. in the case of the large chamber, the deflexions with the wires in air or carbon dioxide are very little different, the former being slightly the greater. In the case of the small chamber, however (see curves A and B), the corresponding deflexion with the wires in carbon dioxide is more than double of what it is when the wires are surrounded by air. Moreover, in fig. 3, for any fixed value of the bridge-current, the deflexion corresponding to any definite pressure is throughout greater in the case of carbon dioxide than in the case of air, while in general, in fig. 2, this is the case only for comparatively low pressures for bridge currents equal to 0.8 and 0.9 amp.

The values of the deflexions on rotation of the plane of

the wires from the horizontal to the vertical are plotted in fig. 4, as ordinates against the respective values of the bridge current as abscissæ, the pressure being throughout adjusted to 760 mm. of mercury. Curves A and B refer to the small chamber, and curves C and D to the large chamber. It is seen that at this pressure the greatest sensitivity of the inclinometer is afforded when the wires are enclosed in a *large* chamber containing *air* (curve D). In such a chamber the sensitivity in both air and carbon dioxide is greater than that characterizing the respective sensitivities



in a chamber such as that employed by Humphrey, in which an inversion of this order of relative sensitivities occurs (curves A and B). Attention may here be directed to the inversion of the relative magnitudes of the respective sensitivities in air and carbon dioxide when the wires are enclosed in the large chamber, and the value of the current is altered. As shown by the point P in fig. 4, in this chamber, for values of the heating current below about 0.73 amp., an enclosure containing carbon dioxide affords the greater sensitivity; above this value of the bridge-current, the greater sensitivity is obtained when the large chamber is filled with air. In the small chamber, no such inversion of the relative magnitude of the respective sensitivities occurs.

All the results may be readily interpreted as follows:—In the large chamber the differential thermal effect experienced by the wires on rotation is conditioned partly by convection effects, and partly by conduction and radiation effects. In the small chamber, convection effects are almost entirely eliminated. For the present purpose radiation effects can be neglected, and attention confined entirely to convection and conduction effects under the various conditions of the experiments.

Consider first the curves corresponding to a current of 0.9 amp. in fig. 2. For pressures less than 350 mm. of mercury (point P) in the large chamber, an atmosphere of carbon dioxide affords the greater sensitivity. This result is analogous to those shown by the curves for the small chamber in fig. 3, and indicates that as the pressure is reduced below about 350 mm. of mercury with a heating current equal to 0.9 amp. differential effects due to convection become relatively diminishingly unimportant compared with differential conduction effects in the chamber. For lower values of the heating current, the pressures corresponding to the intersection of the respective curves become higher, and for heating currents of 0.5 and 0.6 amp., the respective curves for air and carbon dioxide would presumably intersect at points corresponding to pressures greater than atmospheric.

The differential convection effect is conditioned by a variety of factors as the pressure in the large chamber is reduced. Among these are included: (a) the higher temperature of the wire, (b) the diminished density of the gas in the chamber, and (c) the increased velocity of the free convection current from the wires due to (a) and (b). Attention has already been directed to the different slopes of the portions Q P and R P of the curves in fig. 2 for air and carbon dioxide as the pressure in the large chamber is reduced below 760 mm. Interpreted in the light of the formulæ given by King* and by Langmuir† for the free convection loss from a fine heated platinum wire, these results indicate that for air, over the appropriate range of pressures, the value of the product $S\sigma V$, where S is the value of the specific heat of air at constant volume, σ the density of the gas, and V the velocity of the free convection current, is practically constant. For carbon dioxide on the other hand, the value of the product increases as the pressure in the chamber is reduced, the value of V increasing at a greater rate than $S\sigma$ decreases.

* Phil. Trans. A, vol. 214, p. 381 (1914).

† Phys. Rev. vol. xxiv. p. 401 (1912).

It will be clear that the explanation of the characteristics of the various curves for the large chamber in fig. 2 is tantamount to the following. For low pressures and (or) small values of the heating current, the differential thermal effects experienced by the wires are conditioned principally by considerations of conduction losses from the respective wires. For larger values of the heating current and comparatively high pressures, differential convection effects become increasingly important. The respective thermal conductivities of air and carbon dioxide at 0°C. are 5.22×10^{-5} and 3.07×10^{-5} c.g.s. units respectively. For the same small values of the heating current, therefore, the wires when surrounded by air in the large chamber will be colder than will be the case when carbon dioxide is the medium contained in the chamber. It may be anticipated, therefore, that the differential thermal effects are under these conditions less in air than in carbon dioxide. In like manner, for low values of the pressure in the large chamber, the temperature of the wires surrounded by air will be lower than is the case when the chamber is filled with carbon dioxide.

It has been previously shown that dissipation of heat from the hot wire to the surrounding medium occurs directly through a thin layer of stagnant gas surrounding the wire*. As the temperature of the wire is increased, the temperature gradient in, and the thermal conductivity of, this stagnant layer increases. Calculation shows that the thermal conductivity of carbon dioxide increases much more rapidly with temperature than does that of air. Thus, calculating the respective values of the conductivities of carbon dioxide and air at 360°C. , 690°C. , and 1060°C. , (corresponding to the points R, P, and Q respectively in fig. 6, on page 955 later) by extrapolating O. E. Meyer's formula $K = 1.603 \eta_{tc}$, employing Sutherland's formula for calculating η_t we find:—

Temperature (0°C.)	Thermal Conductivity.		Ratio $\frac{K_t}{K_0}$	
	Air.	Carbon Dioxide.	Air.	Carbon Dioxide.
0°	5.22×10^5	3.07×10^5	1	1
360°	8.7	7.6	1.7	2.5
690°	11.4	10.4	2.2	3.4
1060°	13.8	12.9	2.6	4.2

It will be seen that while the respective thermal conductivities of air and carbon dioxide increase rapidly with

* Phil. Mag. vol. xxix. p. 534 (1920).

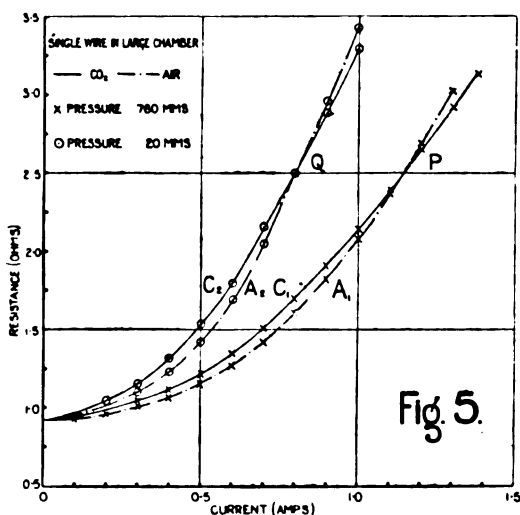
increase of temperature, the rate of increase in the case of carbon dioxide is very much greater than in the case of air. So far as experimental evidence is available *, it is probable that as the temperature of the wires is increased, the ratio of the heat dissipated by conduction to the total heat dissipated from the wires increases. This effect, combined with the greater relative increase in the thermal conductivity of the stagnant layer surrounding the wires in the case of carbon dioxide, leads to the conclusion that with rise of temperature the proportion of heat lost by conduction increases more rapidly in the case of a wire surrounded by carbon dioxide than in the case of one surrounded by air. Alternatively, we may say that, with rise of temperature, the proportion of heat lost by convection increases more rapidly in the case of air than in the case of carbon dioxide. It is therefore to be anticipated that under conditions where differential thermal effects experienced by the wires are determined principally by convection currents, *i. e.*, for large values of the heating current and moderate or large values of the pressure in the chamber, the sensitivity of a hot wire inclinometer in which the wires are surrounded by air would be greater than would be the case with carbon dioxide surrounding the wires. This is in accordance with the results corresponding to the portions Q P and R P of the curves corresponding to a bridge-current of 0.9 amp. in fig. 2. A similar result is shown by the corresponding portions of the curves for 0.8 and 0.7 amp.

The correctness of the view advanced in the preceding paragraph was readily verified by determining the resistance of one of the wires surrounded by either air or carbon dioxide in the chambers. This was done by measuring, by means of a potentiometer, the voltage drop across the wire when a known current was maintained in the wire. The potentiometer readings were calibrated by a Weston cell standardized at the National Physical Laboratory. The pressure within the chamber was adjusted throughout to one or other of the values 760 mm. or 20 mm. of mercury respectively in two series of experiments.

The results obtained when a single wire was enclosed within the large chamber are shown in fig. 5, in which the values of the heating current are plotted as abscissæ against the corresponding resistance of the wire as ordinates. The curves A_1 and A_2 refer to the cases where the single wire was surrounded by air at pressures equal to 760 mm.

* See Barratt, Proc. Phys. Soc. vol. xxviii. part 1, p. 10 (1915).

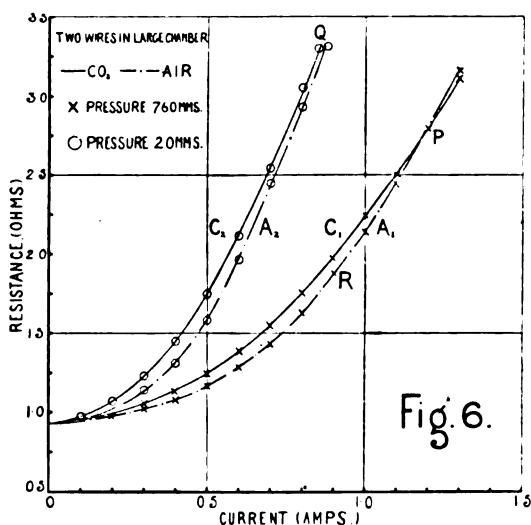
and 20 mm. respectively. The curves C_1 and C_2 have similar reference to the case where the chamber was filled with carbon dioxide. It is seen from curves A_1 and C_1 that for values of the heating current such that the temperature of the wire is below that corresponding to P—about 606°C —the wire when surrounded by carbon dioxide is hotter than is the case when air surrounds the wire. This would be anticipated from the greater value of the thermal conductivity of air compared with that of carbon dioxide. For values of the heating current greater than 1.14 amp. corresponding to P the wire is hotter when surrounded by air. At these temperatures the calculated value of the



thermal conductivity of air is still greater than that of carbon dioxide (see Table on page 952), but the ratio approaches more nearly to equality as the temperature is raised. It is clear, therefore, that the difference in temperature of the wire in the two media is conditioned principally by differences in the respective convection losses at high temperatures, whereas at low temperatures such difference is conditioned principally by differences of conduction losses. At 2 mm. pressure the corresponding curves A_2 and C_2 intersect at Q corresponding very nearly to the same temperature as that represented by P.

The effect of the introduction of a second wire parallel to the first, separated by a distance of 1.5 mm., and heated by

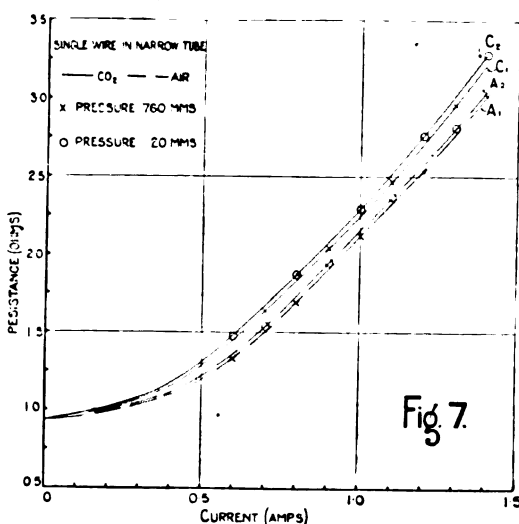
the same current, as in the inclinometer, is seen in fig. 6. The notation of the curves is the same as in fig. 5. The point of intersection of A_1 and C_1 in fig. 6 occurs at a higher temperature than is the case in fig. 5. This indicates that under conditions such that equal total dissipation of energy would occur from the wires in the two cases, the proportion of convection loss to the total loss from a wire would be less in the case of a wire constituting one of a pair disposed as described, than would be the case when one wire alone was heated in the chamber. Results obtained when the pressure in the chamber is reduced to 20 mm. (curves A_2 and C_2 , fig. 6), show that under these conditions differences in the



respective convection effects become still less relatively important, the curves not intersecting within the range of heating currents employed.

In the small chamber as shown in fig. 7, the difference of the temperature in the two cases when a single wire is surrounded by either air or carbon dioxide as shown by the curves A_1 and C_1 , or A_2 and C_2 , is conditioned under all conditions principally by conduction effects. As seen from a comparison of the curves A_1 and A_2 , or C_1 and C_2 , convection losses are practically entirely absent, and the temperature of the wire in one or other gas when heated by a constant current is only very little higher when the pressure is 20 mm. than when the pressure is 760 mm. of mercury.

The curves A_1 and C_1 in fig. 7 are of some interest in another connexion. The fact that a fine platinum wire carrying a constant current becomes heated to different temperatures when the gaseous medium surrounding the wire is altered, forms the basis of Shakespear's katharometer * originally employed for the determination of the degree of purity of hydrogen. Recently the device has found industrial application for determining and recording the percentage of carbon dioxide in flue and other gases †. A Wheatstone bridge device is employed, a pair of arms being constituted of two fine heated platinum wires contained



within chambers filled respectively with the gas to be examined, and a gas of standard composition, the chambers being small so that convection effects are negligible. Carbon dioxide present in flue gases is diluted principally with nitrogen and oxygen, and the gases may be sampled at a temperature of 300°C ., or higher, and subsequently cooled to atmospheric temperature. Now it is evident from fig. 7 that a change from 0 to 100 per cent. in the carbon dioxide content of the flue gas would alter the resistance of the wire immersed in the gas by about 9 per cent. at the most.

* See Proc. Roy. Soc. vol. xcvi. p. 273 (1920).

† See Daynes, Proc. Phys. Soc. vol. xxviii. p. 165 (1921).

Efficient control of combustion processes requires the carbon dioxide content of flue gases to be maintained constant, certainly to within 1 per cent., which would correspond to a change of approximately 0.09 per cent. in the resistance of the wire immersed in the sampled gas. Such a difference of resistance of the wires in the respective chambers would arise owing to a difference of about 0.25° C. in the temperatures of the gases in the respective chambers. Equality or constancy of the difference of temperatures of the gases in the two chambers to within about 0.03° C. is therefore necessary, if the indications of the instrument are to be comparable in accuracy with that easily obtainable (0.1 per cent.) with various forms of gas analysis apparatus in which the carbon dioxide content of the gas is determined by observation of the gas volume before and after the absorption of that constituent.

The author desires to express to Dr. Charles Carpenter C.B.E., his thanks for the provision of facilities for carrying out the work detailed herein.

709 Old Kent Road, S.E. 15.

29 January, 1923.

XCVII. *Cathodo-Luminescence and its Relation to States of Molecular Aggregation.* By J. EWLES, Assistant Lecturer in Physics, Leeds University*.

THE term luminescence seems to have been first introduced by Wiedemann to denote all the cases of re-emission of absorbed energy as light. The absorbed energy may be derived from light (including ultra-violet and infra-red), X-rays, cathode rays, or the radiations from radium.

Although the phenomenon has been the subject of careful investigations for a number of years and a considerable amount of experimental evidence has been obtained, there has yet appeared no satisfactory general explanation of all the facts. Indeed, the evidence on the surface appears to be so complicated and diverse that a statement of the general conclusions is impossible without a certain degree of selection.

* Communicated by Prof. R. Whiddington, M.A., D.Sc.

The following facts, however, emerge as being important :—

I. Nature of spectra.

- (a) All luminescent spectra, however excited, are arranged in bands showing equal frequency differences*.
- (b) An intimate relation exists between the luminescent spectra of a body and the absorption spectra. It seems probable that under similar conditions the one is the complement of the other†.

II. The effect of temperature is very variable.

Dewar‡ found that many substances which luminesce at ordinary temperatures do not do so at the temperature of liquid air, and *vice versa*.

At low temperatures the broad bands break up into narrower bands§. There is an upper limit of temperature beyond which luminescence || ceases.

III. The effect of impurities is very marked.

- (a) Pure substances do not luminesce¶.
- (b) Luminescence results from admixture of a small amount of impurity called by Bruninghaus the Phosphorogene**.
- (c) Different impurities affect the colour of the luminescence differently by affecting the relative intensity and distribution of the bands††.
- (d) There is always an optimum of luminescence corresponding to a certain small and fixed percentage of impurity‡‡.

* Wood, 'Physical Optics.' Nichols and Merritt, *Phys. Rev.* 1912. Howes and Wilber, *ibid.* 1917. Nichols and Howes, 1916 & 1918, *ibid.* Mrs. F. G. Wick, *ibid.* 1918. Nichols and Wilber, *ibid.* 1920.

† H. and J. Becquerel & K. Onnes, *Konink. Akad. Wetensch. Amsterdam*, 1909. J. Becquerel, *C. R.* 1910.

‡ Dewar, *Proc. Roy. Soc.* xiv. (1895).

§ J. Becquerel, *C. R.* 1907. H. Becquerel, *C. R.* 1907.

|| Lenard and Klatt, *Ann. der Phys.* xv. (1904). Nichols and Wilber, *Phys. Rev.* 1921.

¶ Urbain and Bruninghaus, *Ann. Chem. et Phys.* 1909. Mourello, *C. R.* cxxiv. 22, 1237. Nichols, Howes, and Wilber, *Phys. Rev.* 1918. Nichols, Howes, and Wick, *ibid.* 1919. Grüne, *Ber. Deutsch. Chem. Gesell.* 1904.

** *Loc. cit.*

†† Mourello, *C. R.* cxxvi., and Becquerel, *C. R.* cvii.

‡‡ Lenard and Klatt, *Wied. Ann.* 1889.

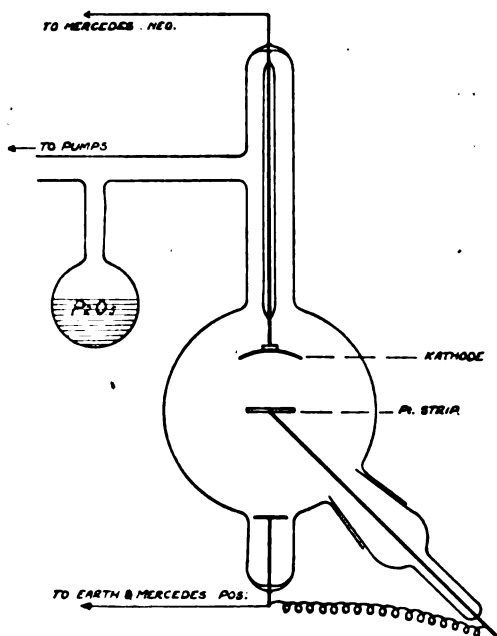
IV. The state of aggregation of the substance is a determining factor in the nature or very existence of luminescence and equally in the character of absorption bands*.

This is discussed at length later in this paper.

V. With increasing frequency of the exciting radiation, *i. e.* greater energy, the luminescent spectra extend further into the violet.

Experiments were begun with the object of determining whether the luminescence excited by cathode rays appears only when the rays acquire a minimum speed, *i. e.* whether a definite quantum of energy is required to excite the luminescence. It was thought that such an investigation might lead to some indication as to the nature of the processes giving rise to luminescence.

Fig. 1.



Some twenty metallic oxides and several other substances were examined. The substances were deposited in a thin layer on a strip of platinum mounted in a vacuum flask at the focus of a concave cathode (fig. 1). The tube was excited by a

* Wood, 'Physical Optics.' Hodgson, Phys. Rev. 1918. Nichols and Wilber, Phys. Rev. 1917.

Mercedes electrostatic machine, and the voltage applied controlled by the pressure of the residual gas and measured by a Kelvin and White electrostatic voltmeter. It was found that the cathodo-luminescence did not appear until the potential applied to the tube reached a certain critical value.

That is, for each substance, the cathode rays must possess a minimum amount of energy before luminescence is excited.

Details of the results are shown in Table I.

TABLE I.

Substance.	Colour of Luminescence.		Minimum voltage for excitation.
MoO	Blue	faint.	3400
ZrO	Mauve	strong.	1200
Fe ₂ O ₃	{ Greenish- yellow }	{ faint.	{ 1500 (see also Table II.,
CaO	Yellow	strong.	1050
CaS	Yellow	strong.	950
BaO (impure)	Yellow	strong.	2150
BaO (AR)	Yellow	strong.	700
Cr ₂ O ₃	Blue	faint.	3800
WO ₃	Blue	faint.	5200
BiO ₃	Orange	faint.	1900
MnO ₂ (pyrolusite) ..	GY → RY	faint.	3400
SrO	Blue	faint.	1350
CuO	Violet	faint.	1100
Cu ₂ O ..	Violet	faint.	1400
Sb ₂ O ₃	Whitish	faint.	1700
PbO	Whitish	faint.	1900
SnO	Whitish	{ moderately strong. }	1425
SiO ₂	Blue	brilliant.	750
Al ₂ O ₃	Blue and pink.		{ 580-650 (according to sample).
MgO } ZnO }	See Table II.		

In each case the potential corresponding to first appearance with increasing voltage and to disappearance with decreasing voltage was observed many times.

One is well aware that the possibility of determining the exact point of appearance or disappearance is limited by the sensitiveness of the eye, and the minimum voltages obtained must in all cases be too high.

In many cases, however, the luminescence came in so sharply as to leave no doubt as to the existence of a very definite minimum. More exact measurements are in progress which do not depend on the sensitiveness of the eye.

Nichols and Howes (Phys. Rev. 1921) have plotted curves, showing intensity of luminescence against voltage, which show the existence of a minimum voltage for luminescence. They do not appear to have taken into account the variation of the cathode ray current with voltage, so that the actual values obtained are hardly reliable.

Examination of the results shown in Table II. brings out the following points :—

(1) For each substance showing cathodo-luminescence there is a critical speed of rays required to excite it which is characteristic of the particular substance.

(2) A comparison of the minimum energy required in the case of similar oxides shows that no simple relation exists between the energy change and the atomic numbers of the metals. This suggests that the transformation is not atomic.

(3) Nor does there appear to be any simple relation between the minimum energy and the heat of dissociation or formation such as would be expected on the suggestion put forward by Baly and others that the change involved is a chemical one.

It was found, indeed, that even with the same chemical substance, all precautions being taken against the entry of new impurities, the method of preparation has a marked effect on the critical energy, colour and intensity of the luminescence. Each sample shows some difference, often very marked, in the colour, intensity, and critical speed for excitation.

These results show how the state of aggregation of a substance affects its luminescence. This is in agreement with the observations of many previous workers on cathodo- and other types of luminescence.

Levy (Röntgen Soc. Journ., Jan. 1916) showed that the colour and intensity of the fluorescence of barium platino-cyanide is different in the two crystalline states and in the amorphous state.

M. B. Hodgson (Phys. Rev., Dec. 1918) showed that the X-ray luminescence of calcium tungstate depends on its crystal structure.

Baly and Tryhorn (Phil. Mag. xxxi.) find that the position and depth of the absorption bands of pyridine and salicylaldehyde vary with the concentration.

Waentig (*Zeitschr. Phys. Chem.*) found that the phosphorescent alkaline-earth sulphides passed when rubbed into coloured non-luminous powders, which change is accompanied by a decrease of volume and an absorption of energy.

Phil. Mag. Ser. 6. Vol. 45. No. 269. May 1923. 3 Q

TABLE II.

Zinc oxide, from pure zinc *.

Method of Preparation.	Colour of Luminescence.	Minimum voltage for excitation.
1. Sublimed from zinc arc.	Green.	650
2. Zinc hydroxide pptd. from cold solution and ignited	Bluish-white.	850
3. Sample from (2) heated for one hour at 1200° C.	Yellowish-green.	350
4. Zinc hydroxide pptd. from hot solution and ignited.....	Red and green together.	400
5. Zinc ignited in air	Green.	580
6. Zinc nitrate ignited.....	Orange.	650
7. Sample from (6) heated at one spot to incandescence	Heated part green. } Unheated part orange. }	550
8. Zinc carbonate ignited...	Green.	725
9. Sample from (8) heated to incandescence	Green.	400

* Analytical reagent manufactured by British Drug Houses Ltd.

Magnesium oxide, from magnesium AR.

1. Smoke from burning Mg deposited on a hot platinum strip	Rose and sky-blue.	650
2. Smoke from burning Mg deposited on a cold platinum strip	Rose and sky-blue.	1200
3. Mg(OH) pptd. and ignited	Sky-blue.	1200
4. Mg(NO ₃) ₂ ignited	Faint blue.	1700

Natural crystalline Fe₂O₃.

1. Small crystals about 1 mm. dimensions	{ Faint red; blue at higher voltages. }	4000
2. Crushed to powder in an agate mortar	{ Whitish-blue; phosphorescent for some minutes. }	1000
3. Crushed to very fine powder and then "rolled" in an agate mortar.....	No fluorescence.	—

Silicon.

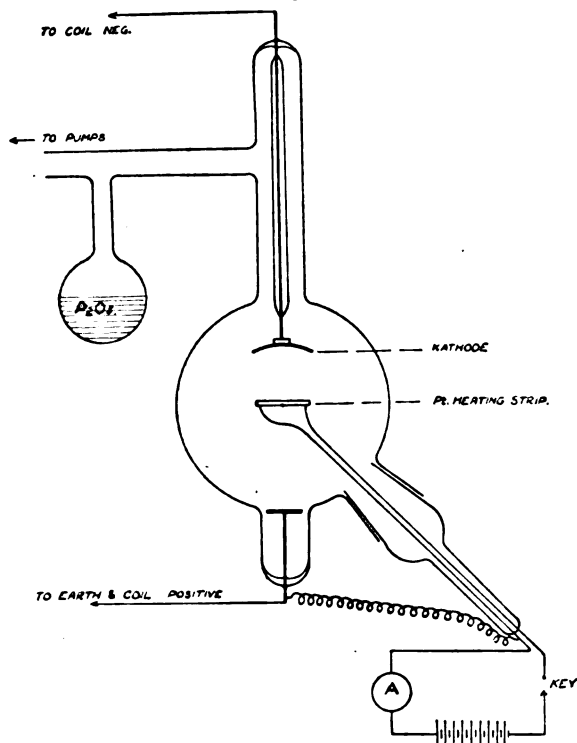
1. Amorphous	Whitish-yellow.	1600
2. Crystalline	Red.	2400

Imof (*Phys. Zeitschr.* 1917) finds a minimum-sized crystal necessary for tribo-luminescence.

Lenard and Klatt showed that the alkaline-earth sulphides lose their luminescent properties if subjected to high pressures. See also Beilby ('Aggregation and Flow of Solids'), Sect. xi.; S. E. Shepherd (*Illum. Eng. Lond.*, June 1917); T. R. Merton (*Chem. Soc. Journ.*, Jan. 1914); Farnau (*Le Radium*, June 1914).

Following up the train of thought suggested by these results, substances were taken which were known or could be shown to undergo a change of molecular aggregation if heated beyond a certain temperature. For example, quartzite exists in two forms, α and β , differing in density and refractive index, a reversible change from the α to the β form taking place at 575°C . Such substances were examined with a view to determining whether any change takes place in the cathodo-luminescence at the temperature

Fig. 2.



of transformation. The substances were deposited in a thin layer in the middle of a strip of platinum which could be raised to any desired temperature by the passage of a steady current. The magnitude of the current, measured by a Cambridge and Paul ammeter, gave the temperature, the strip having been previously calibrated by determining the current required to melt various salts of known melting-points. The calibration curve was checked at the higher temperatures by a Cambridge optical pyrometer.

The platinum strip acted as the anode (see fig. 2) so that the rays from the cathode could be fired at the substance deposited on it. The source of high potential in these experiments was an induction-coil which could be switched on and off rapidly so as to avoid, as far as possible, heating the substance by the rays.

In order to test whether the momentary flash of cathode rays appreciably raised the temperature of the substance, the intensity of the rays was varied by altering the residual gas-pressure and by varying the current in the primary of the coil. No appreciable variation of the temperature of disappearance could be detected.

In those cases where the transformation temperature was not already known, this was determined by the Roberts-Austen differential heating or cooling curve method. In this method the substance under test is heated in an electric furnace by the side of a standard substance which is known to undergo no transformation. Thermocouples of platinum and an alloy of 90 per cent. platinum and 10 per cent. rhodium are imbedded in each and connected in opposition to a sensitive galvanometer. The temperature of the sample is obtained by a third thermocouple. Any molecular transformation absorbs or generates heat, so that the temperature of the test material when the transformation takes place lags behind or advances on that of the standard substance, and this difference in the temperatures is at once indicated by a deflexion of the differential galvanometer. For the suggestion of this method and help in carrying it out, I owe thanks to H. S. Houldsworth, of the Fuel Department of Leeds University.

Experiments on fourteen different substances gave the remarkable result that above the temperature of transformation the cathodo-luminescence disappears.

The results are summarized in Table III.

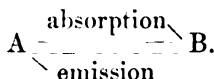
The remarkably close agreement shown in the above table between the transformation temperature and the temperature of disappearance of the luminescence indicates an intimate relation between the processes involved in the molecular rearrangement and the emission of luminescence. The fact that the sample of alumina which showed no transformation also showed no luminescence is highly significant.

The evidence seems sufficient to warrant the hypothesis that luminescence is a manifestation of the energy change involved when a substance changes from one state of molecular aggregation to another. Any theory of luminescence must take into account the intimate relation between

TABLE III.

Substance.	Nature of Transformation.	Temp. of Transfn.	Disappearance of Fluorescence.
Zinc oxide	{ Sudden change of density and resistance. }	700°	700°
Magnesium oxide	Slow change to periclase.	{ 900° (begins).	930°
Zirconium oxide	Slow change of density.	700°	730°
Alumina (by ignition)..	Change of density.	1060°	1060°
NaOH		299°-6	293°
KOH		248°	242°
Wollastonite (CaSiO ₃).	Pseudo-wollastonite.	1197-1232° (according to the rate of heating).	1240°
Calcium orthosilicate (2CaO)SiO ₂	{ Large volume change with powdering. }	675°	680°
Cyanite	Change to sillimanite.	1300°	1330°
Quartzite.....	{ Change of μ and 0.5% volume expansion. }	575°	575°
K ₂ SO ₄		580-599°	600°
LiSO ₄		575°	570°
CaSO ₄		666°	680°
Alumina (pptn. from Al ₂ (SO ₄) ₃ by NH ₄ OH and ignition	{ No transformation occurs. }	1065°	No fluorescence.

luminescent and absorption spectra pointed out earlier in this paper. Indeed, it seems justifiable to make the assumption, as most recent writers on the subject have done, that the two processes correspond to different aspects of the same reversible change, the system absorbing in one direction and emitting luminescence in the other. Thus:—



The fundamental difference in the general formula expressing the distribution of frequency in band spectra, $=A+Bm+Cm^2$, involving only positive powers of m , and the general formula for line spectra, involving negative powers of m , may be taken to indicate a corresponding difference in the structure of the systems whose changes of energy give rise to the two different kinds of spectra.

The results of the experiments described above suggest that the system in the case of luminescent and absorption spectra is an aggregate of molecules. The extremely important part played by impurities in the nature and even existence of luminescence mentioned earlier helps to form an

idea of the possible structure of the radiating system. Sir J. J. Thomson (Phil. Mag., May 1914) shows that certain special types of molecules containing oppositely charged atoms may act as electrical doublets, and by virtue of their strong electrostatic fields possess the power of condensing a large number of other molecules round them. This action, he maintains, will involve molecular rotations when the system is being formed or rearranged. We might imagine, then, the bipolar nucleus of impurity, with its cluster of surrounding molecules, as playing the same part in the emission or absorption of band spectra as the Bohr atom, with its positive nucleus and surrounding electrons, plays in the production of line spectra.

The changes of energy of the electrons in the atom giving rise to line spectra are here replaced by changes of the molecular rotational and oscillational energy, as the aggregate is formed or rearranged, giving rise to the emission or absorption of band spectra. This view gives a physical aspect to the Schwartzschild development of the band-spectra formula. This author has shown that the general band-spectrum formula can be arrived at by applying quantum considerations to the changes of rotational and oscillation energy of molecular doublets.

The theory of luminescence here advanced seems to offer a reasonable explanation of all the experimental data. It explains why, as Baly (Phys. Rev. 1921) pointed out, the frequencies in absorption spectra are multiples of a common molecular frequency characteristic of the substance.

Lenard and Klatt (*Ann. der Physik*, 1904) found that in certain cases a flux was necessary for luminescence. The action of the flux may be explained as facilitating molecular rearrangement.

In phosphorescence we may suppose that the stimulus brings about the reversible change in the direction involving absorption, the return to the former state with the emission of energy as phosphorescence going on for some time after the stimulus is removed.

The phenomenon of thermo-luminescence observed by Wiedemann, namely, that certain substances did not show luminescence while being stimulated but after removal of the stimulus and subsequent heating gave out luminescence, is accounted for by supposing that the stimulus brings about molecular rearrangement into a metastable condition and that subsequent heating is necessary to reverse the change.

The very variable effect of temperature follows directly from the theory. Temperature determines the state of

aggregation, and the fact that a substance may not luminesce above or below a certain temperature indicates that any change that can occur will be in a direction involving absorption.

Taking the minimum energy required to excite cathodoluminescence, as determined in the above experiments, to represent the quantum of energy required to transform the molecular aggregate, and assuming equipartition of this energy among the constituent molecules of the aggregate, it should be possible from a knowledge of this energy and the molecular heat of transformation to determine the number of molecules composing the aggregate. For example:—

The critical potential for zinc oxide varies with the sample, as indicated above, from 350 to 850 volts. The energy per electron corresponding to this is 5.565×10^{-10} erg and 15.421×10^{-10} erg respectively.

The heat of transformation of zinc oxide is 4.41 kg.-cals. per gram-molecule, *i. e.*

$$\frac{4.41 \times 10^3 \times 4.2 \times 10^7}{60.6 \times 10^{22}} = 3.06 \times 10^{-13} \text{ erg per molecule,}$$

which gives a molecular aggregate of 1818 in the lowest case and 4271 in the highest. The writer is well aware, for the reasons stated earlier, of the very approximate nature of these numbers. Experiments are in preparation, however, for a more accurate determination of the minimum cathodic energy and a parallel determination of the energy of transformation, from which it is hoped to obtain fairly reliable results as to the number of molecules in an aggregate. It is hoped also to obtain an estimate of a minimum possible number of molecules which can form a crystal, in various cases.

Summary.

I. A generalized survey of the chief results obtained by previous workers on luminescence.

II. Experiments with cathode rays on a number of substances indicate that each substance showing cathodoluminescence requires a minimum speed of cathode rays to excite the luminescence. This speed appears to be characteristic of the substance, but depends also on the state of aggregation.

III. The temperature at which cathodo-luminescence disappears coincides, in the case of all substances examined,

with the temperature at which a molecular transformation takes place.

IV. A general theory of luminescence suggested by these results is put forward.

In conclusion, I wish to express my very great indebtedness to Professor R. Whiddington, who suggested the original problem, for his continual advice and encouragement throughout.

Physics Department,
The University, Leeds.

XCVIII. *Some Observations on the Ignition of Combustible Gases by Electric Sparks.* By J. D. MORGAN, M.Sc.*

IT has been shown by calculations that the amount of heat energy that must be imparted to cause ignition of a combustible gas mixture can vary greatly with the conditions under which the heat is supplied (Taylor Jones, Morgan, & Wheeler, *Phil. Mag.* vol. xliii. Feb. 1922). In making the calculations, it was assumed that ignition is a thermal process involving the raising of a certain volume of the gas to a certain temperature, and that the heat is communicated from the source to the gas by conduction. The heat energy required in the source to produce ignition is least when the heat is imparted instantaneously. When the rate of heat supply is less a greater quantity of heat must be given to the gas before ignition can occur. It was also shown that variations in the shape or linear dimensions of the heat source would result in variations of the heating effect.

The sparks used for ignition of combustible gases are of two kinds (capacity and inductance sparks) which differ notably in temperature and duration. The spark produced by a single discharge from an electrostatic condenser across a gap between stationary electrodes has, judged by its luminosity, a very high temperature, and is of extremely short duration; whilst that produced during separation of a pair of contacts in an inductive circuit has a lower temperature and is usually of relatively long duration.

The results of previous experimental work on spark

* Communicated by Prof. E. Taylor Jones.

ignition are characterized by remarkable diversity. Nevertheless, there emerges the general conclusion that to ignite a given gas mixture a larger amount of heat must be imparted by an inductance spark than by a capacity spark, and the differences observed are broadly such as are consistent with the hypothesis that ignition is a thermal process.

At first sight it would appear to be easy to submit the theoretical deductions above mentioned to quantitative tests. Closer examination shows, however, that serious and possibly insuperable difficulties lie in the way, and it becomes doubtful whether additional experiments can do more than confirm the general agreement that already exists between the thermal hypothesis and experimental results. Further, it would appear that development of the thermal hypothesis is more likely to depend on an accumulation of indirect evidence than on direct demonstration.

It has been shown by Patterson and Campbell (*Proc. Phys. Soc. of London*, vol. xxxi. pt. iv. June 15th, 1919) that the energy required for ignition of a given gas mixture by a capacity spark (instantaneous heat source) may be a widely variable quantity. In expressing their results they correlated the spark energy and the sparking voltage of the gap at which the igniting sparks were produced. No explanation of the results was suggested.

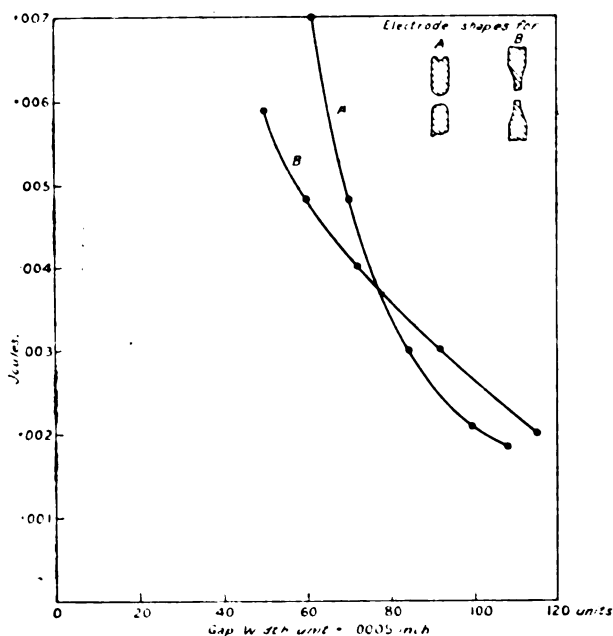
The fact observed by Patterson and Campbell is one of considerable practical importance in connexion with the ignition of gases in internal combustion-engines. It appeared to the writer to be one of theoretical importance also. He decided therefore to repeat and extend their experiments with a view to comparing the results with the thermal hypothesis of ignition.

The curve A, fig. 1, was obtained from experiments on a mixture of methane and air (about 8.8 per cent. methane). In the same diagram is shown the shape of the spark-gap electrodes. The sparks were produced by discharge of a variable condenser across a gap of variable width. Charging of the condenser was effected by means of an induction-coil acting through a thermionic valve. To find each point on the curve the condenser was adjusted to a particular value and the gap width was increased until ignition occurred. In expressing the results, the energy in the system prior to the occurrence of the spark is taken as a measure of spark-energy, and this is correlated with spark-gap width.

The conditions of the experiments though apparently simple are really very complex. At least three important

variables are involved, and each of these affects the results in a probably indeterminate manner. These variables are (1) the spark-length, (2) the configuration of the gas region immediately adjacent to the spark, and (3) the area of cooling surface presented by the electrodes to the incipient flame. Probably the effect of variation of spark-length is negligible in comparison with the other two, and attention has therefore been confined to them. It does not appear to be possible to separate the effects of these two without incurring other serious difficulties. That a change in the

Fig. 1.

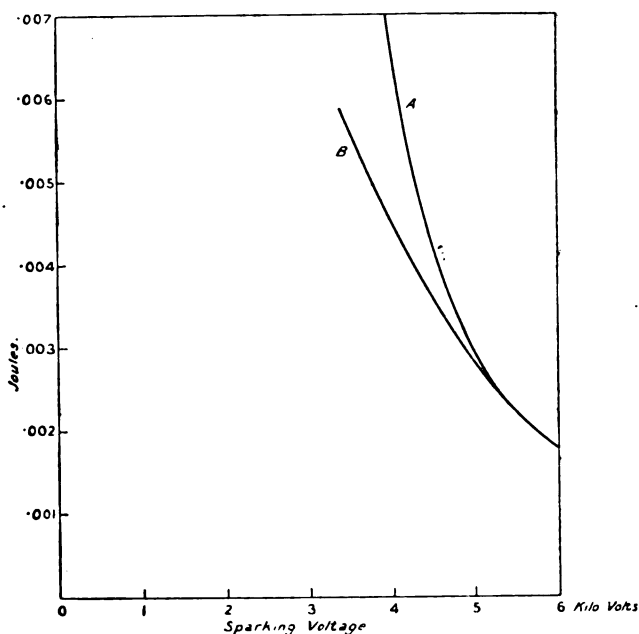


configuration of the gas region adjacent to the spark has an important effect, is evident from curve B. To obtain this curve the shape of the electrodes was altered as shown in the diagram, but the curvature at the sparking position was kept the same as before in order to minimize as much as possible any consequent variation of the sparking voltage. It might be said that the alteration of shape also resulted in an important reduction of cooling effect by the electrodes, but there is reason to believe that the difference between the curves A and B is less due to cooling than to increase in

the volume of gas immediately adjacent to the spark, though it must be admitted that variation in the cooling effect of the electrodes is involved in the results.

It will be noticed that the curves intersect. This is due to the fact that at the larger gap-widths the sparking voltages of the two gaps were not quite the same. When the spark energy is plotted against spark voltage, the two curves coincide at their lower ends as shown in fig. 2. Similar results were obtained from experiments on coal-gas and blast-furnace gas.

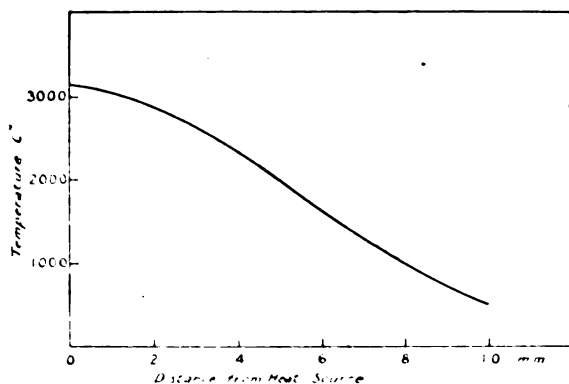
Fig. 2.



The problem to be considered is as to whether or not such results as those shown in figs. 1 and 2 are consistent with the hypothesis that ignition depends on raising a certain volume of the gas to a temperature not less than the ignition temperature. The calculations recorded in the paper previously referred to afford a basis for a definite affirmative answer. It was shown that the temperature wave, resulting from the instantaneous discharge at a point in the gas of a certain quantity of heat, assumed, after an interval of time,

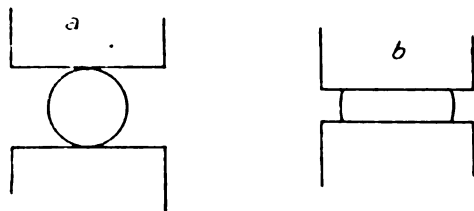
the form shown in fig. 3, the volume of gas in which no part was at a temperature below 700° being then a maximum. To correlate the experimental results with the curve in fig. 3, two assumptions will be made. Wheeler has shown that the initial form of a flame resulting from the ignition of a gas by a spark is approximately of the same shape as would result from rotating a V about an axis through its ends, the axis being also the axis of the spark. This shape suggests

Fig. 3.



that the cooling effect of the electrodes is such that the most effective portion of the spark is at or near the centre of its length. The first assumption is, therefore, that the heating effect produced by a short linear spark will not be greatly different from that of a point. The second assumption (made to simplify the problem) is, that the gap electrodes are formed with flat ends, and the thermometric conductivity of the electrodes is the same as that of the gas

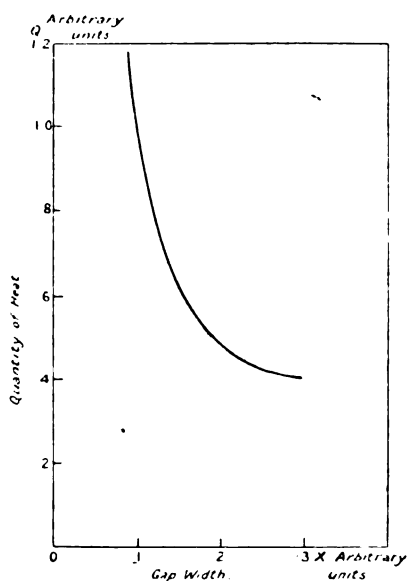
Fig. 4.



in which the spark passes. The diagrams in fig. 4 show two positions of the gap electrodes, and the circular lines indicate the boundaries of two equal volumes of gas contained

between the electrodes. It will be evident that to raise the boundary of the volume of gas shown by *b* to the same temperature (say, $700^{\circ}\text{C}.$) as the boundary of the gas volume shown by *a*, will require a larger quantity of heat in the source. Indicating the gap-width by *x* and the quantity of heat required in the source by *Q*, the relationship between *Q* and *x* has been calculated from the curve shown in fig. 3. The result is shown in fig. 5. It will be seen that the general form of the curve is the same as that of the experimental curves A shown in figs. 1 and 2.

Fig. 5.



Though no quantitative comparison can be made between the hypothetical and actual curves, the agreement of general form affords important evidence in support of the thermal hypothesis. The differences which must be made in the hypothetical curve to compensate for the assumptions made in obtaining the curve are not such as will cause any alteration in the character of the curve.

Incidentally, the experiments serve to illustrate the important fact that the heat required to cause ignition of a given gas mixture is a quantity that can vary greatly with the experimental conditions, even when sparks of the same type are used. The results obtained by different investigators

can never be comparable unless carried out with identical apparatus. At one time the diversity of results was the cause of much perplexity. It has since become increasingly apparent that this perplexity was due mainly to a misconception of what was implied by the supposition that ignition is a thermal process.

Experimental.—When capacity or condenser sparks are used in ignition experiments it is usual to calculate the spark energy from the expression $\frac{1}{2} CV^2$, where C is the capacity across the gap and V the sparking voltage of the gap. Knowing that the results of this procedure could be misleading, the matter was subjected to a close examination, and some interesting effects were observed. At first it was the intention to use a number of small glass condensers of about equal capacity, and arrange for one or more to be connected in parallel with the gap in the explosion apparatus. These were calibrated by charging to a known potential and discharging through a ballistic galvanometer. Then a small spark-gap was arranged in series with the galvanometer circuit, and the calibration experiment was repeated. As was anticipated, the discharge through the galvanometer was less than when the gap was not present. It was noticed, however, that the ratio of the two discharges was not a very regular quantity and was not the same for all the condensers, and the calibration graph correlating quantity of discharge across the gap and the total capacity of the condensers in operation showed well-marked "steps." If these condensers had been used in the explosion experiments and the spark energy had been expressed, as usual, by $\frac{1}{2} CV^2$, the true results would have been masked by irregularities due to the behaviour of the condensers. Condensers with other solid dielectrics were tried, and in all cases similar effects were observed. Finally, a variable air-condenser was constructed, and with this the irregularities disappeared. The ratio of the discharges under the two conditions above mentioned was perfectly regular and consistent. Its value for one gap setting was '87. In figs. 1 and 2 the energy was calculated from the known values of C and V , and as the results were only required for comparative purposes, the correction for "gap effect" was not applied. The experience gained in this investigation showed that with condensers having solid dielectrics serious discrepancies could arise, and that these could be avoided successfully by the use of air-condensers.

As already stated, the condensers were charged at a relatively slow rate in the explosion experiments, from an induction-coil acting through a thermionic valve. By

this means irregularities in the sparking voltage due to "impulsive" effects* were avoided. Nevertheless, serious irregularities in the sparking voltage of the gap were observed, and these for a time caused much trouble. When the gap was exposed to the open air of the laboratory it behaved with great regularity and consistency. But when put into operation within the explosion apparatus no two discharges occurred across the same gap-width at the same voltage, and often the sparking voltage required to produce a spark was double the normal sparking voltage of the gap. Different metals were tried in the gap-electrodes, namely, platinum, steel, nickel, and brass, and all gave similar results. The procedure followed in each ignition experiment was to evacuate the explosion chamber and let in a charge of previously prepared gas mixture from a holder, the gas on its way from the holder being caused to pass through a drying agent. Ignition of the charge was effected at atmospheric pressure. As causes of the irregularities in the sparking voltage, electrode surface condition and deficient ionization of the gas were suspected. The experiments made to ascertain the cause did not, however, lead to any definite results. The balance of evidence appeared to indicate that the trouble was due to deficient ionization, but the discovery of a simple remedy made it unnecessary to examine the matter further. It was found that by reducing the gap to a relatively small amount after each introduction of a fresh charge, and causing one or two small sparks to pass (insufficient to have any appreciable effect on the gas) the irregularity could be almost entirely removed. With experience in the use of the apparatus it became easy to detect "over-voltages," especially when an ammeter was arranged in the primary circuit of the induction-coil and the primary current adjusted so that the secondary discharges were only sufficient to raise the condensers to the normal sparking voltage of the gap.

The unit of gap measurement adopted was .0005 of an inch, and in the methane-air experiments it became possible to obtain a high degree of accuracy and consistency. With a given capacity in the system, the gap settings necessary to cause ignition in a dozen successive trials would not vary by more than one unit of gap-width. All the points on the curves shown in fig. 1 were obtained under these conditions. Using coal-gas and blast-furnace gas, the results were less regular and the gap settings necessary to cause ignition could not be ascertained to less than .001 of an inch.

* "Impulsive Sparking Voltages," *Phil. Mag.* vol. xli, March 1921.

XCIX. *The Theory of the Trevelyan Rocker.*
By E. G. RICHARDSON, M.Sc. (East London College) *.

WHEN Arthur Trevelyan, Esq. (as he is described in the Transactions of the Royal Society, 1831), accidentally discovered † that an iron fork laid on a block of lead gave rise to musical sounds, he set to work to devise a model which should best exhibit the effect, and produced the well-known prismatic block of copper having a groove in its under surface so that it would rock on the ridges, the other point of support being a knob at the end of a thin round handle. Sir John Leslie suggested a theory of the action, which was accepted by Trevelyan and remained unchallenged, save by Forbes, until recently. Trevelyan found it necessary to have the ridges very smooth and clean, but the lead was best roughened. Heat being communicated to the lead by the copper, the rugosities of its surface were supposed to expand, to push up each ridge in turn, and then to contract as the heat diffused through the lead, the rocking being due to inequality of inertia of the portions of the rocker on opposite sides of the ridge, or to a difference in condition of the lead on either side of the line of contact with the ridge, causing a lateral movement. Faraday ‡, as a result of experiments with various pairs of metals, went further and said that the success of the experiment depended on the difference of conductivity of the two metals; the hot one must readily transfer its heat to the cold one, but the heat must not be able to diffuse rapidly into the latter, but remain near the point of contact causing local expansion; it was immaterial which one formed the rocker, cold lead would vibrate on a hot copper block.

However, Forbes § was unable to substantiate Faraday's conclusions, and advanced a new theory that the phenomenon showed evidence of a repulsion taking place when heat is transferred from a body of high conductivity to one of low. Seebeck || and Tyndall ¶ put Forbes' argument against Faraday's hypothesis thus: (1) the greater the expansion

* Communicated by Prof. C. H. Lees, F.R.S.

† A German workman had discovered it independently some years before (*vide* Gilbert, *Pogg. Ann.* xxii. p. 323, 1806).

‡ *Journ. Roy. Inst.* 1831.

§ *Trans. Roy. Soc.* 1833.

|| *Pogg. Ann.* li. p. 1 (1840).

¶ *Phil. Mag.* vii. p. 223, and viii. p. 1 (1834).

of the block, the greater the effect, but (2) the greater the conductivity of the block, the greater the expansion ; therefore (3) the greater the conductivity, the greater the effect (whereas lead, a bad conductor, exhibits the effect best). They pointed out, however, that the expansion in (1) is vertical, whereas that in (2) is *total* ; so that Forbes' objection to the original theory is invalidated. Further, Tyndall set aside Forbes's own hypothesis, because he succeeded in making a substance vibrate on one of equal conductivity, *e. g.* copper on copper, provided that the metal beneath was reduced to the points of wires or the edges of thin laminæ, so that lateral conduction in the underlying metal was prevented.

In further support of the theory that the phenomenon was maintained by heat, Page* made a light rocker vibrate on two rails connected to the terminals of an electric battery, the heat being produced by the thermoelectric effects at the points of contact.

Finally, Davis† embellished this theory by a mathematical investigation, in which, by considering the rate of transfer of heat to the cold metal, he obtained the height to which the surface is raised by a given difference of temperature and period of rocking, and so calculated the difference of temperature necessary to produce vibrations at a given rate in a rectangular parallelepiped with two parallel ridges. He concluded from his analysis that a difference of 50° to 100° C. would be sufficient to cause the rocker to vibrate 225 times per second. This result is in fair agreement with the earlier experiments of Sondhauss‡, who found minimum differences of temperature from 30° to 80° C., the minimum increasing with the time of swing.

The subject then lay dormant for nearly 50 years. Quite recently Chuckerbutti§ has succeeded in obtaining some actual values for the amplitude, or height to which the ridge rises, and for the corresponding frequency of the vibration, by a mirror carried on a thin rod, rolling on the back of the rocker. By reflecting light from this mirror on to a moving photographic plate, the motion was exaggerated several thousand times, and some excellent photographs obtained. By measuring these the amplitude could be calculated ; the

* Sill. Journ. p. 105, 1850.

† Phil. Mag. xlv. p. 296 (1873).

‡ Pogg. Ann. cxv. pp. 71 & 177 (1873).

§ Proc. Indian Assoc. Sci. vi. p. 143 (1921).

frequency was found by tuning a sonometer to unison with the note. Mr. Chuckerbutti thinks that the old theory is inadequate, and that when the rocker has settled down to a steady musical tone, "the *elastic vibrations* of the rocker and handle-bar play an important part, and eventually entirely displace any such simple rocking movement as may occur in the earlier stages of the experiment."

The work described below was undertaken with a view to an investigation of the relative merits of the two rival theories (referred to in this paper as the "gravity" and the "elastic" theory) more thorough than that of Mr. Chuckerbutti. He gives only 7 values of the frequency and corresponding amplitude, whereas by the method to be described some 350 were obtained.

Method of observing Amplitude and Frequency.

A block of lead with rounded top is screwed down to the bench. A small hole is bored through the rocker, through which a thick steel knitting-needle is thrust and held in position by a small screw, so that the needle lies horizontally about the centre of the rocker, when the latter rests with its two ridges across the lead block. The end of the needle or indicator is observed through a microscope, which can be quickly brought to bear on the indicator by adjusting a couple of wooden wedges placed between the bench on which it rests and the barrel of the microscope. The light by which the field of the microscope is illuminated comes from a little electric lamp placed behind the slits of a stroboscopic disk, driven by an electric motor. When the disk is rotating, therefore, the illumination is intermittent, and its period may be made to coincide with that of the rocker by finding the *fastest* speed of the motor which makes the end of the needle appear stationary in the microscope. This speed was measured by a stroboscopic vibrator in conjunction with the usual print of differently spaced circles of dots, pasted on the disk. By using a micrometer eyepiece, and setting the disk slightly out of step with the rocker, the amplitude at the end of the indicator could be readily observed as the needle appeared to move slowly up and down.

A third observation was made at the same time as the other two, *i. e.* that of the temperature of the rocker, by a method due to Sondhauss. A hole bored in the back is filled with mercury, into which the bulb of a 0° - 360° C.

thermometer, supported above, is placed, without touching the vibrating rocker.

By placing a glass micrometer scale on the object table of the microscope and focussing, it is found that 1 cm. on the eyepiece scale corresponds to an actual distance of $\cdot 016$ cm. in the object plane, and as the length of the indicator to the centre of the rocker is in each case 10 cm., this corresponds to an amplitude of $\cdot 0016$ ($2a$) at the ridge, where $2a$ is the distance between the ridges. The magnification is therefore from 1000 to 2000 times.

Fig. 1.

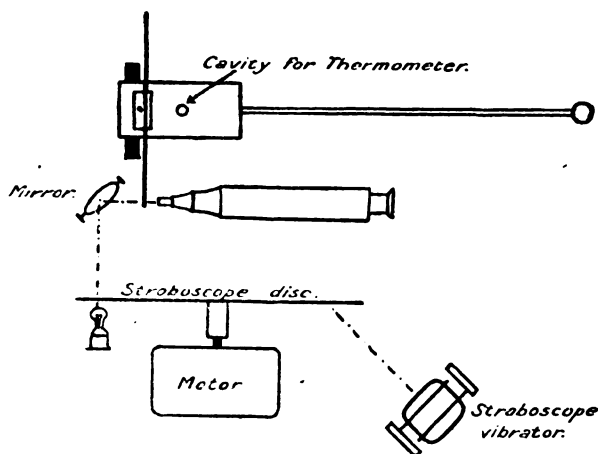


Diagram to show arrangement of apparatus (from above).

The first few tests with this apparatus gave amplitudes about 10 times those of Chuckerbutti, though the frequencies were of the same order. It was thought that perhaps the indicator exaggerated the vibrations, as it should do if their period were near its own. The needle was thereupon clamped at its centre, and its free vibrations (transverse) observed in the apparatus. Their frequency was found to be 168, which considerably exceeded any values obtained from the prismatic rockers. To make sure, two other tests were made. Firstly, another needle $\cdot 48$ cm. thick was passed through a parallel hole in the rocker so that its end and that of the original needle ($\cdot 19$ cm. thick)

could be simultaneously examined in the microscope. When the rocker was vibrating, the two rose and fell with the same amplitude, period, and phase (when examined by the method described above), showing that it was the vibrations of the rocker that were being observed, not the free vibrations of the needles, which, being of different thicknesses, would have exhibited different amplitudes when vibrating "freely" under resonance from the rocker*. Secondly, a galvanometer mirror was fixed on the back of the rocker so as to reflect light from a lamp on to a scale a metre above. When the rocker vibrated, the spot of light on the scale was drawn out into a band, whose length could be roughly determined†. The value of the amplitude calculated from this rather inaccurate measurement was of the same order as that obtained simultaneously from the needle under the microscope.

One reason why Mr. Chuckerbutti's values are low may be that he used a wooden block to press his rotating needle on to the rocker, and this probably acted as a restraint. A needle and wooden block having been lightly laid on the rocker (the other end of the wood being supported), it was found that the amplitude increased by $1\frac{1}{2}$ to 2 times when the needle and block were carefully lifted off the block by strings, and the "restraint" thus removed.

The Gravity Theory.

If M = mass of rocker, K its spin-radius, ϕ ang^r deviation from the vertical, $2a$ = distance between ridges, the equation of motion is

$$MK^2 \frac{d^2\phi}{dt^2} = -Mga.$$

An integration for $\frac{1}{4}$ -time-period gives

$$K^2\omega = agT, 4$$

if R is the amplitude at a ridge, ω = angular velocity,

$$\frac{1}{2}\omega = \phi_{\max.}/\frac{1}{4}T \quad \text{or} \quad \phi_{\max.} = R/2a, \quad \text{and} \quad \omega = 4R/aT;$$

therefore
$$T^2 = \frac{16RK^2}{a^2g}.$$

* This test was also applied to the simple rockers described below, but at various frequencies between 50 and 200 no resonance was detected.

† A device first used qualitatively by Tyndall.

If n stand for the frequency, this equation may be written

$$n^2 R = \frac{a^2 g}{16 K^2}^*.$$

We see, then, that the gravity theory requires the amplitude and frequency to be connected by the formula $n^2 R = \text{constant}$, whereas, if the vibrations are elastic, the frequency should be independent of the amplitude when the latter is small, but dependent on the length of the rocker and handle.

Results with Prismatic Rockers.

Two prisms were used, 12 cm. and 6 cm. long respectively, provided with two interchangeable handles, also of copper, 32 cm. and 24 cm. long, ending in brass knobs.

The observations are recorded in the following tables:—

$$2a = \cdot 5 \text{ cm.}$$

K^2 (for an isosceles triangle, height b , base c , about an axis perpendicular to plane through vertex) $= \frac{c^2}{24} + \frac{b^2}{2} = 3\cdot 98 \text{ cm.}^2$,

whence
$$n^2 R = \frac{a^2 g}{16 K^2} = \cdot 96.$$

(The actual amplitude is $\cdot 0008$ of that observed at the eyepiece.)

TABLE I.
Large Rocker and Long Handle.
($n^2 R$ calculated $= \cdot 96$.)

Temp. C.	R in cms.	n .	$n^2 R$.	Temp. C.	R in cms.	n .	$n^2 R$.
110	$4\cdot 8 \times 10^{-4}$	55	1\cdot 45	130	$4\cdot 6 \times 10^{-4}$	$43\frac{1}{2}$	1\cdot 06
185	12\cdot 0 "	34	1\cdot 38	100	4\cdot 8 "	47	1\cdot 06
120	4\cdot 0 "	56	1\cdot 25	105	4\cdot 8 "	53	1\cdot 32
190	9\cdot 6 "	38	1\cdot 38	135	4\cdot 0 "	55	1\cdot 21
150	8\cdot 8 "	40	1\cdot 41	150	7\cdot 2 "	47	1\cdot 58
125	5\cdot 6 "	58	1\cdot 88	190	9\cdot 6 "	$37\frac{1}{2}$	1\cdot 33
165	8\cdot 0 "	44	1\cdot 55	170	8\cdot 8 "	47	1\cdot 94
175	1\cdot 6 "	69	0\cdot 74	175	8\cdot 4 "	46	1\cdot 76
205	10\cdot 0 "	$37\frac{1}{2}$	1\cdot 76	175	10\cdot 0 "	41	1\cdot 72

* This is the formula which Chuckerbutti derived, tested, and found wanting.

TABLE II.
Large Rocker and Short Handle.

Temp. C.	R in cms.	<i>n</i> .	<i>n</i> ² R.	Temp. C.	R in cms.	<i>n</i> .	<i>n</i> ² R.
240	10.4×10^{-4}	41	1.74	130	4.8×10^{-4}	47	1.06
200	8.0 "	45	1.62	145	4.8 "	56	1.60
100	4.0 "	58	1.34	105	1.6 "	44½	0.32
190	5.6 "	53	1.57	140	4.0 "	58	1.34
180	4.8 "	53	1.48	200	1.6 "	65	0.67
150	3.6 "	59	0.35	150	5.6 "	54	1.64
155	4.4 "	58	1.47	120	4.0 "	57	1.30
105	4.0 "	56	1.25	160	5.6 "	51	1.45
200	10.0 "	39	1.52	120	2.2 "	52	0.59
225	9.6 "	40	1.53	190	6.4 "	43	1.01

TABLE III.
Small Rocker and Long Handle.

Temp. C.	R in cms.	<i>n</i> .	<i>n</i> ² R.	Temp. C.	R in cms.	<i>n</i> .	<i>n</i> ² R.
180	3.6×10^{-4}	60	1.29	190	7.2×10^{-4}	16½	1.48
160	6.4 "	17½	1.96	120	2.8 "	68	1.29
160	8.0 "	40	1.28	155	8.8 "	41	1.48
200	2.4 "	49	0.58	180	2.0 "	51	0.52
115	4.0 "	61	1.48	105	2.0 "	90	1.62
175	2.8 "	61	1.04	128	8.0 "	39	1.20
115	2.4 "	76	1.38	105	2.0 "	93	1.42
130	4.0 "	53	1.13	105	3.2 "	61	1.58
145	5.6 "	45	1.13	180	12.8 "	34	1.48
185	5.6 "	54	1.62	160	4.0 "	65	1.69
115	3.2 "	61	1.19	215	6.4 "	46	1.35
130	3.2 "	58	1.06	180	2.0 "	88	1.55
155	3.6 "	58½	1.22	110	3.2 "	60	1.15

TABLE IV.
Small Rocker and Short Handle.

Temp. C.	R in cms.	<i>n</i> .	<i>n</i> ² R.	Temp. C.	R in cms.	<i>n</i> .	<i>n</i> ² R.
105	7.2×10^{-4}	40	1.15	200	12.0×10^{-4}	32½	1.28
240	12.0 "	36	1.55	160	6.4 "	47½	1.28
160	12.0 "	37½	1.68	100	2.0 "	92	1.70
180	3.2 "	61	1.18	170	4.8 "	60	1.73
150	5.6 "	53	1.57	190	3.6 "	70	1.76
195	2.4 "	70	1.17	100	2.0 "	98	1.93
150	3.2 "	56	1.00	150	4.0 "	59	1.38
95	2.0 "	92	1.70	180	3.2 "	70	1.57
120	2.4 "	96	2.21	185	4.0 "	58	1.35
200	9.6 "	34	1.11	190	4.0 "	50	1.40
165	7.2 "	41½	1.23	200	10.4 "	37½	1.48
140	3.2 "	65	1.35				

From these results it may be seen that :

(1) n^2R is fairly constant, though rather higher than the calculated value. If a graph be drawn, it is found that the values of n^2R for the small rocker lie fairly along the curve $n^2R = 1.2$.

(2) an alteration of the length of the handle does not affect the average value of n^2R , nor does it affect the range of frequency.

(3) amplitudes are greater at higher temperatures, though this is probably dependent on the excess temperature of the copper over the lead, not on the actual temperature of the former.

Results with Simplified Rockers.

The difference between the calculated and average experimental values of n^2R obtained from prismatic rockers may be due to an imperfect knowledge of the value of K for such a shape. Accordingly a simpler form was devised, consisting of a cylindrical rod of copper with a groove cut from one end to within $\frac{1}{2}$ in. of the other. It had a peg in the centre of one end, so that, by resting the peg on a knife-edge, the bar rocked very nearly about its axis.

In the following tables (V.-VII.), frequencies greater than 130 were more conveniently found by sonometer. Most of those lying between 100 and 130 were estimated by both methods to serve as a check; they differed by less than 1 per cent. In estimating the constancy of the values of n^2R in the last column, it must be remembered that amplitudes are correct only to 0.4×10^{-4} .

The form of this simple rocker makes it easy to calculate its frequency under *elastic* vibration, treating it as a bar supported at both ends. These vibrations may be longitudinal, torsional, or transverse.

(1) Longitudinal :

$$\text{velocity} = \sqrt{Y/\rho} = 3 \times 10^5 \text{ cm./sec. at } 100^\circ \text{ C.}^*$$

(2) Torsional :

$$\text{velocity} = \sqrt{n/\rho} = 2 \times 10^5 \text{ cm./sec. at } 100^\circ \text{ C.}$$

Dividing either of these velocities by $2l$, where l is the length of the bar, we get frequencies running into thousands

* The values of Y and rigidity are from Wertheim Pogg. *Ann.* lxxviii. p. 381 (1849).

TABLE V.

Cylindrical Rocker, $\frac{1}{2}$ in. diameter.

$$2a = .32 \text{ cm.}; r = .625 \text{ cm.}; K^2 = \frac{1}{2}r^2 = .195 \text{ cm.}^2;$$

$$\text{whence } n^2R = 8.0.$$

(a) Length 22 cm. Weight 240 gms.

Temp. C.	R in cms.	n .	n^2R .	Temp. C.	R in cms.	n .	n^2R .
210	5.6×10^{-4}	173	16.8	105	2.4×10^{-4}	248	14.7
145	4.0 "	198	15.7	145	4.0 "	193	15.0
115	1.6 "	270	11.7	130	4.0 "	201	16.3
165	4.8 "	188	17.0	115	3.6 "	234	19.7
145	4.8 "	206	20.3	105	3.2 "	240	18.4
140	4.0 "	225	20.3	95	3.2 "	253	20.5
120	3.6 "	240	20.7	140	5.6 "	192	20.2
130	4.4 "	211	19.6	120	2.4 "	206	10.3
110	3.2 "	234	17.5	145	4.0 "	197	15.5
105	4.8 "	173	14.4	190	4.0 "	167	11.2
170	4.8 "	180	15.6	170	3.2 "	187	11.2
140	2.4 "	201	10.1	160	3.2 "	200	12.8

(b) Length 17 cm. Weight 190 gms.

160	3.2×10^{-4}	211	14.2	160	4.0×10^{-4}	200	16.0
150	3.2 "	222	15.7	145	3.2 "	222	15.7
135	3.2 "	236	13.9	120	2.4 "	255	15.6
150	3.2 "	222	15.7	105	2.0 "	263	13.8
125	2.0 "	234	11.0	160	3.2 "	222	15.7
115	2.0 "	248	12.3	160	3.2 "	217	15.0
195	3.2 "	197	12.4	170	4.0 "	201	16.2
170	3.2 "	211	14.5	200	0.8 "	345	9.6
115	1.6 "	259	10.3	135	3.2 "	228	16.6
125	2.0 "	234	10.9	115	0.8 "	345	9.6

(c) Length 12 cm. Weight 140 gms.

115	1.6×10^{-4}	240	9.2	185	1.8×10^{-4}	60	6.6
125	2.4 "	200	9.6	130	2.8 "	184	15.5
90	2.8 "	168	7.7	110	3.2 "	196	9.9
90	2.4 "	130	7.6	120	2.0 "	200	8.0
110	2.4 "	182	7.9	170	8.0 "	132	13.9
170	12.8 "	68	5.9	100	2.4 "	192	8.8
160	4.0 "	177	12.5	115	1.6 "	220	8.2
205	3.2 "	188	11.7	240	12.0 "	90	9.7
160	12.0 "	90	9.6	160	10.4 "	92	8.8
100	2.4 "	188	8.0	115	1.6 "	216	11.4
200	24.0 "	16	7.1	120	6.4 "	140	13.4

TABLE VI.

Cylindrical Rocker, $\frac{3}{4}$ in. diameter.

$$2a = .32 \text{ cm. ; } r = .95 \text{ cm. ; } K^2 = \frac{1}{2}r^2 = .45 \text{ cm.}^2 ;$$

$$\text{whence } n^2R = 3.5.$$

(a) Length 23 cm. Weight 520 gms.

Temp. C.	R in cms.	n.	n^2R .	Temp. C.	R in cms.	n.	n^2R .
120	8.0×10^{-4}	57	2.6	90	2.4×10^{-4}	140	4.7
105	4.0 "	92	3.4	170	4.0 "	114	5.2
90	3.2 "	114	4.1	135	2.4 "	140	4.7
130	3.2 "	126	5.1	140	8.0 "	60	2.9
180	2.4 "	123	3.6	125	4.0 "	98	3.8
165	3.2 "	111	3.9	200	4.0 "	92	3.4
150	3.6 "	114	4.8	180	2.4 "	130	4.1
135	2.4 "	133	4.2	165	5.6 "	74	3.1
145	2.0 "	154	4.7	215	6.0 "	80	3.7
115	5.6 "	89	4.4	165	4.0 "	96	3.7

(b) Length 17 cm. Weight 400 gms.

170	4.8×10^{-4}	70	2.3	115	6.0×10^{-4}	62	2.8
140	5.6 "	75	3.1	110	2.4 "	160	6.2
130	3.2 "	117	4.4	150	4.0 "	133	7.1
120	3.2 "	133	5.7	150	3.2 "	142	6.5
100	2.4 "	137	4.5	105	2.8 "	109	3.3
180	3.2 "	120	4.6	95	3.2 "	109	3.8
160	3.2 "	133	5.7	180	4.0 "	136	7.4
130	3.2 "	108	3.7	130	3.6 "	109	4.3
115	4.0 "	89	3.2	120	4.4 "	81	2.9
130	6.4 "	62	3.4	115	4.8 "	67	2.2

(c) Length 12 cm. Weight 280 gms.

190	2.0×10^{-4}	133	3.5	150	4.0×10^{-4}	139	7.2
175	2.8 "	112	3.5	130	4.0 "	150	9.0
160	2.8 "	124	4.3	110	2.4 "	120	3.5
125	8.0 "	52	2.3	150	3.6 "	91	3.0
120	1.6 "	154	4.7	135	2.8 "	137	5.3
105	4.0 "	107	4.6	120	6.4 "	66	2.8
100	3.6 "	104	3.9	150	5.6 "	64	2.3
180	2.4 "	130	4.1	105	3.2 "	100	3.2

TABLE VII.

Cylindrical Rocker, 1 in. diameter.

 $2a = \cdot 32$ cm.; $r = 1\cdot 27$ cm.; $K^2 = \cdot 78$ cm.²;whence $n^2R = 2\cdot 0$.

(a) Length 23 cm. Weight 970 gms.

Temp. C.	R in cms.	n .	n^2R .	Temp. C.	R in cms.	n .	n^2R .
180	$12\cdot 0 \times 10^{-4}$	35	1\cdot 5	105	$2\cdot 4 \times 10^{-4}$	108	3\cdot 0
160	9\cdot 6 "	53	2\cdot 7	140	2\cdot 4 "	64	1\cdot 5
145	8\cdot 0 "	57	2\cdot 8	120	3\cdot 2 "	66	1\cdot 4
130	4\cdot 8 "	63	1\cdot 9	105	4\cdot 0 "	64	1\cdot 6
100	3\cdot 2 "	65	2\cdot 1	180	2\cdot 4 "	98	2\cdot 3
95	2\cdot 4 "	78	1\cdot 5	150	4\cdot 4 "	66	1\cdot 9
200	4\cdot 4 "	63	1\cdot 7	185	16\cdot 0 "	32	1\cdot 6
185	3\cdot 6 "	72	1\cdot 9	175	13\cdot 6 "	35	1\cdot 6
160	8\cdot 0 "	56	2\cdot 5	165	7\cdot 2 "	46	1\cdot 5
130	4\cdot 0 "	65	1\cdot 7	130	4\cdot 0 "	66	1\cdot 7
95	4\cdot 0 "	63	1\cdot 6	90	3\cdot 2 "	70	1\cdot 6

(b) Length 17 cm. Weight 720 gms.

145	$5\cdot 6 \times 10^{-4}$	63	2\cdot 2	115	$2\cdot 8 \times 10^{-4}$	90	2\cdot 3
130	2\cdot 4 "	80	1\cdot 5	116	3\cdot 6 "	80	2\cdot 3
125	1\cdot 6 "	96	1\cdot 5	110	2\cdot 4 "	92\frac{1}{2}	2\cdot 0
180	22\cdot 4 "	30	2\cdot 0	110	2\cdot 0 "	102	2\cdot 1
170	8\cdot 0 "	41	1\cdot 3	135	8\cdot 0 "	49	1\cdot 9
160	6\cdot 4 "	47	2\cdot 6	120	3\cdot 2 "	74	1\cdot 7
150	3\cdot 2 "	66	1\cdot 4	115	4\cdot 0 "	80	2\cdot 6
155	4\cdot 0 "	60	1\cdot 2	110	2\cdot 4 "	109	2\cdot 9
145	4\cdot 4 "	75	2\cdot 5	115	5\cdot 6 "	60	2\cdot 0
100	2\cdot 4 "	70	1\cdot 2	135	12\cdot 0 "	52	3\cdot 0
145	4\cdot 0 "	68	1\cdot 8	120	8\cdot 8 "	56	3\cdot 4

(c) Length 12 cm. Weight 520 gms.

140	$5\cdot 2 \times 10^{-4}$	53	1\cdot 4	135	$3\cdot 2 \times 10^{-4}$	66	1\cdot 4
130	1\cdot 6 "	112	2\cdot 0	120	2\cdot 4 "	100	2\cdot 4
200-160	2\cdot 4 "	88	1\cdot 9	105	1\cdot 6 "	106	1\cdot 8
190	16\cdot 0 "	30	1\cdot 4	195	15\cdot 6 "	40	2\cdot 5
170	12\cdot 0 "	35	1\cdot 5	170	9\cdot 6 "	44	1\cdot 8
135	2\cdot 8 "	80	1\cdot 8	160	2\cdot 4 "	88	1\cdot 9
120	2\cdot 4 "	91	2\cdot 0	145	4\cdot 0 "	62	1\cdot 5
105	1\cdot 6 "	109	1\cdot 8	170	6\cdot 4 "	46	1\cdot 3
100	4\cdot 4 "	82	2\cdot 9	160	5\cdot 6 "	53	1\cdot 6
180	3\cdot 4 "	72	1\cdot 8	110	1\cdot 2 "	98	1\cdot 1
110	2\cdot 0 "	93	1\cdot 7	115	2\cdot 4 "	90	1\cdot 9

As none of those in the tables exceeds 350, these kinds of vibrations are out of the question.

(3) Transverse :

$$N = V_{\text{long}} \frac{9}{8} \frac{K}{l^2} \text{ is the lowest frequency possible.}$$

The calculated values for n (transverse) are given below:—

TABLE VIII.
Summary of Results for Cylindrical Rockers.

Radius r in cms.	Length l in cms.	n^2R .		Calculated Transverse Frequency n .		Experimental Range of n .	
		Calc.	Experi- mental average.	At 100°.	At 200°.		
·625	22	8·0	16·1	304	227	270	to 173
"	17	"	13·7	508	380	345	to 197
"	12	"	9·5	1004	765	240	to 60
·95	23	3·5	4·0	472	423	140	to 57
"	17	"	4·3	865	773	160	to 62
"	12	"	4·2	1735	1555	154	to 52
1·26	23	2·0	1·9	622	357	108	to 32
"	17	"	2·0	1135	1020	109	to 30
"	12	"	1·8	2282	2075	112	to 30

It can be seen that the calculated and experimental values of n^2R are in agreement, save in the first two lines (unaccountably), and that the actual range of frequencies is considerably below that required by elastic vibrations (transverse).

The effect of varying the width of the groove while the diameter and length of the bar were kept constant was next examined.

According to the "gravity" formula, n^2R should be proportional to a^2 . The first two sections of Table IX. give good confirmation of this, as the average value of n^2R is quadrupled when the width of the groove is doubled; when the latter is increased half as much again, as in (c), the average value of n^2R is only increased in the ratio 37 : 22, instead of 9 : 4. Rockers with wide grooves are difficult to start, especially if heavy, and do not oscillate well.

It has long been known that pressing or weighting the bar raises the pitch, because the rocker cannot oscillate so far; observations made during the above experiments show that the amplitude is correspondingly reduced.

TABLE IX.

Rod 1.9 cm. diam., $13\frac{1}{2}$ cm. long.(a) $2a = .24$ cm.

Temp. C.	R in cms.	<i>n</i> .	n^2R .	Temp. C.	R in cms.	<i>n</i> .	n^2R .
160	9.6×10^{-4}	45	1.9	170	8.8×10^{-4}	45	1.8
135	10.4 ..	40	1.7	100	5.6 ..	56	1.8
100	3.2 ..	83	2.2	95	4.8 ..	86	4.3
135	5.6 ..	60	2.0	170	9.6 ..	45	1.9
140	1.6 ..	137	3.0	130	4.8 ..	60	1.7
105	4.8 ..	63	1.0	210	24.0 ..	24	1.4
130	19.6 ..	34	2.3	110	11.2 ..	45	2.4
110	3.2 ..	84	2.2	140	1.6 ..	120	2.3
135	5.6 ..	78	3.4	145	20.2 ..	35	2.4
175	10.4 ..	43	1.9	100	2.8 ..	89	2.2

Average value of $n^2R = 2.2$; calculated 2.0.(b) $2a = .48$ cm.

130	1.6 ..	228	10.4	170	3.2 ..	150	7.4
230	4.0 ..	150	9.0	190	5.6 ..	139	10.8
145	5.6 ..	170	13.4	200	4.8 ..	142	9.7
170	2.4 ..	151	5.5	205	5.6 ..	147	12.1
180	8.4 ..	92	6.7	190	5.2 ..	149	11.5
	2.4 ..	132	4.2	—	2.4 ..	146	5.1

Average value of $n^2R = 8.8$; calculated 7.9.(c) $2a = .32$ cm.

150	2.8 ..	137	5.2	120	6.4 ..	66	2.8
115	3.2 ..	117	4.4	115	3.2 ..	100	3.2
190	7.2 ..	55	2.2	170	11.2 ..	51	2.9
170	6.8 ..	59	2.4	135	3.2 ..	100	3.2
150	5.6 ..	64	2.3	120	6.4 ..	66	2.8
135	2.8 ..	133	5.0	170	24.0 ..	35	2.9
120	3.2 ..	137	6.0	125	6.4 ..	62	2.5
136	8.0 ..	60	2.9	115	4.8 ..	117	6.6
125	4.0 ..	110	6.3	95	3.2 ..	107	4.0

Average value of $n^2R = 3.7$; calculated 3.5.

Harmonics of the simple vibration have also been observed in the microscope. Sondhauss and Chuckerbutti's experiments show that these are due to the independent vibration on one ridge alone, taking place at the same time as the more usual rocking from ridge to ridge.

Vibration of the lead block was prevented as far as possible during the above experiments. The intensity of the sound does not depend merely on the amplitude of the rocking, but is amplified by the block, if the latter is in a

condition to do so. Using a hollow lead cylinder for the rocker to work on, Dinkler* found the character of the sound changed by putting weights inside the former.

Conclusion.

The results show that the formula— n^2R constant for a given rocker—satisfies the observed phenomena fairly well. As n^2R has been shown to be proportional directly to a^2 , and inversely to K^2 , it is to be concluded that the gravity theory is the more correct one. Such deviations as occur are at small amplitudes (less than about .0002 cm. for the simple form of rocker), and it is possible that some other form of oscillation is to be found here. No common form of elastic vibration, whether longitudinal, torsional, or transverse, can be present, as the frequencies are not of the required order, nor do they vary with temperature in the manner required by the theory of elastic vibrations.

Finally, the author wishes to express his obligation to Prof. C. H. Lees, of East London College, for bringing Mr. Chuckerbutti's paper to his notice, and for valuable ideas, utilized in this work.

C. On the Theory of δ -Radiation.

By P. L. KAPITZA †.

WHEN an alpha particle strikes a solid body, electrons are emitted from the place of collision and form the so-called δ -radiation. The explanation of the phenomenon is usually given as follows:—

When the particle penetrates into the body, it loses its kinetic energy in ionizing atoms of the body. The liberated electrons possess certain speeds, and after several collisions may escape from the surface. These escaped electrons form the δ -radiation. Such a consideration, however, gives only the general picture of the phenomenon, and is insufficient to provide a basis for any numerical calculations. But if we consider the phenomenon purely from a statistical point of view, we can easily obtain some numerical values for the speeds and numbers of electrons in the δ -radiation.

Let us first assume that the alpha particle, when stopped, liberates all its energy to heat up a very small volume of the body. It can be easily calculated that the temperature at this place of local heating may reach several thousand

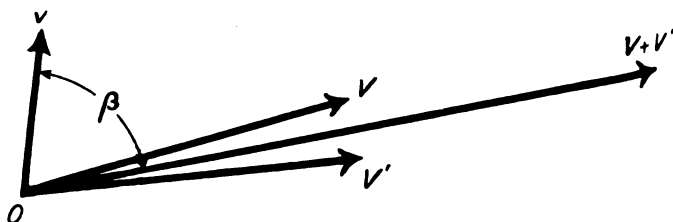
* *Repertorium de Phys.* iv. p. 131 (1868).

† Communicated by Sir Ernest Rutherford.

degrees. From the heated surface of the body, thermionic emission will take place. This thermionic emission is the δ -radiation. This process will last a very short time, due to the fact that the heat will quickly dissipate into the body; but it will be shown in this paper that the δ -radiation calculated from such a picture of the phenomenon gives the right value both for the number of electrons emitted and for their speeds.

Let us suppose that the collision between an α -particle and an atom takes place at O (see fig. 1); then the relations

Fig. 1.



which hold between the velocities of the α -particle before and after collision (written V and V' respectively) and the velocity v of the liberated electron are

$$M(V - V') = mv, \quad . \quad . \quad . \quad (1)$$

$$\frac{1}{2} M(V^2 - V'^2) = \frac{1}{2} mv^2, \quad . \quad . \quad . \quad (2)$$

where M is the mass of the α -particle and m the mass of the electron. Equation (2) may be re-written as

$$M(V - V')(V + V') = mv^2,$$

where the left-hand side of the equation is a scalar product of two vectors. If we call the angle between these vectors β and substitute $(V - V')$ from (1) we have

$$\cos \beta = \frac{v}{V + V'}.$$

Now it is known that an α -particle loses by ionization only a very small portion of its energy, and maintains its direction of motion practically unaltered. Thus we may say that $V + V'$ is practically equal to $2V$, and thus

$$\cos \beta = \frac{|v|}{2V}. \quad . \quad . \quad . \quad (4)$$

If we assume a definite speed for the α -particle, the value of the speed of the electron can be calculated for a given value of β . The results of such calculations are shown in Table I.

TABLE I.

Speeds of the ionized electrons, in volts.

β .	Distance from the end of the α -ray range.		
	7 cm.	3.5 cm.	1.5 cm.
0°	4190	2620	1340
30°	3150	1900	1005
60°	1048	630	335
80°	126	76	40
85°	32	19	10
90°	0	0	

The energy of the ionized electron is expressed in volts for α -particles with ranges 7.0, 3.5, 0.5, and 1.5 cm. in air. Now, if the α -particle at each collision loses energy corresponding to a fall of potential of 40 volts, we see from the table that the value of β for the liberated electrons will lie between 85° and 80°. This means that the velocity of the liberated electron is very nearly perpendicular to the path of the α -particle. If this were so, the electrons produced by an α -particle striking a surface vertically could never escape from that surface without an alteration in the direction of their velocity. Such an alteration would only be produced as a result of inter-electronic collisions.

These collisions would result in a transference of energy from electron to electron, and thus after the passage of an α -particle we have a great number of electrons moving with different speeds and in different directions. This process of the interchange of energy between the electrons will result in the liberation of electrons from the surface.

Now we shall make an attempt to calculate the amount of δ -radiation to be expected, using the known constants of emission formula of Richardson.

From the ordinary data of thermionic emission, we know what is the chance for an electron to escape from the body if it has the average kinetic energy corresponding to a certain temperature. We may assume that after the passage of the α -particle into the solid the ionized electrons remain in a cylinder of small cross-section and possess kinetic energy equal to that lost by the α -particle. This energy is dissipated along the radius of this cylinder according to the ordinary laws of thermal conductivity, while from the cross-section of the cylinder which coincides with the surface of

the body electrons are emitted according to Richardson's law.

The above assumptions are, however, open to criticism. In the first place, the Richardson formula is only true when a Maxwell distribution of electron velocities exists. In our problem this will not be the case, but it is quite probable that, using the Richardson formula, we shall obtain results which are of the correct order of magnitude. In the second place, immediately after the passage of the α -particle only a few thousands of electrons possess very large kinetic energy, and the application of thermal-conductivity constants which have only a statistical mean value is open to criticism in the case of a small volume. But if we bear in mind that in practice we deal with the average value of δ -radiation produced by a very large number of collisions, then the adoption of the ordinary thermal conductivity is probably nearly correct.

Let us take the path of the α -ray as the axis of a cylindrical system of coordinates. Let also the α -particle enter the body at right angles to the surface. Then, in the first moment after the passage of the α -particle, all the energy yielded to the body will be included in a cylinder which we shall take as infinitely thin. In this way we may state the initial conditions of the problem. Thus if T is the temperature, t the time, and r the distance from the axis, we have:

$$t = 0, \quad T = 0, \quad r \neq 0;$$

$$t = 0, \quad T = \infty, \quad r = 0.$$

The ordinary thermal-conductivity equation may be written

$$r \frac{\partial T}{\partial t} = \frac{K}{cd} \frac{\partial}{\partial r} r \frac{\partial T}{\partial r} \dots \dots \dots (5)$$

where K , c , and d are the thermal conductivity, thermal capacity, and density of the body respectively. To find a particular solution of this equation which will satisfy the initial conditions, we shall introduce a new variable u such that

$$u = \frac{r^2}{t} \dots \dots \dots (6)$$

Equation (5) will then take the form

$$u \frac{dT}{du} = - \frac{4K}{cd} \frac{d}{du} u \frac{dT}{du} \dots \dots \dots (7)$$

and this, after integration, gives

$$T = D \int_0^{\frac{cd}{4K} \cdot \frac{r^2}{t}} \frac{e^{-y}}{y} dy, \dots \dots \dots (8)$$

where D is a constant.

By differentiating this particular solution with respect to t , we find a solution which will satisfy the initial conditions :

$$T = \frac{D}{t} e^{-\frac{cd}{4K} \cdot \frac{r^2}{t}}. \dots \dots \dots (9)$$

To determine the constant D in this expression (9), we may express the fact that an amount of heat Q , equivalent to the amount of energy lost by the α -particle per unit length of path, passes through unit length of the surface of a cylinder coaxial with the origin during the time from $t=0$ to $t=\infty$. This is done by the expression

$$Q = -2\pi K \int_0^\infty r \frac{\partial T}{\partial r} dt. \dots \dots \dots (10)$$

Thus, using (9) and performing the integration, we get

$$D = \frac{Q}{4\pi K}; \dots \dots \dots (11)$$

and the required solution of equation (5) is therefore

$$T = \frac{Q}{4\pi K t} e^{-\frac{cd}{4K} \cdot \frac{r^2}{t}}. \dots \dots \dots (12)$$

According to the laws of thermionic emission, the number of electrons emitted per unit surface of the heated body during one second is given by

$$N = AT^{\frac{1}{2}} e^{-\frac{b}{T}}, \dots \dots \dots (13)$$

where A and b are experimentally-determined constants*. Now, if we sum the right-hand side of the expression (13) over all possible values of r and t , the number of electrons emitted by the collision of an α -particle will be

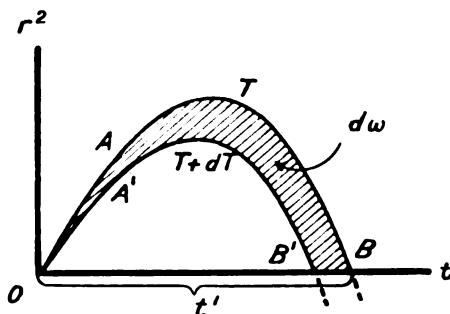
$$N = \int_0^\infty \int_0^\infty \pi A T^{\frac{1}{2}} e^{-\frac{b}{T}} dr^2 dt. \dots \dots \dots (14)$$

To perform the integration in (14), by substituting for T

* See Richardson's book, 'The Emission of Electricity from Hot Bodies.'

from (12) we get a very complicated expression. But the difficulty can be overcome in the following way:—Let us take two coordinate axes for the variables r^2 and t , as shown in fig. 2. Then the meaning of our integration may be

Fig. 2.



interpreted as follows. Each surface element of the area included between the two axes will be multiplied by

$$f(r, t) = \pi A T^{\frac{1}{2}} e^{-\frac{b}{T}}$$

and the whole summed. Now let us divide the surface into elements ($d\omega$) over which the temperature may be taken as constant. For this purpose we take T as constant in the expression (12), and, varying r^2 and t , we draw the curve OAB . Afterwards we draw another curve $OA'B'$ for a temperature equal to $T + dT$. Then the hatched surface $OABB'A'$ will be equal to the element of the surface ($d\omega$) with constant temperature.

It is easy to see that

$$d\omega = \frac{d \int_0^{t'} r^2 dt}{dT}, \quad \dots \dots (15)$$

where t is the uppermost limit of integration determined from the point of intersection of the curve OAB with the axis t . The value of t is obtained from (12) by putting $r^2 = 0$. Thus

$$t' = \frac{Q}{4\pi K T}. \quad \dots \dots (16)$$

If we introduce in (15) the value of r^2 from (12), we get

the following expression for $d\omega$:

$$d\omega = \frac{Q^2}{8\pi^2 KcdT^3}, \quad \dots \dots \dots (17)$$

and the number of electrons emitted will be

$$dN = AT^{\frac{b}{T}} e^{-\frac{b}{T}} \pi d\omega = \frac{AQ^2}{8\pi Kcd} T^{-5/6} e^{-\frac{b}{T}} dT. \quad \dots (18)$$

After performing the integration with respect to T from 0 to ∞ we get

$$N = \frac{1}{16\sqrt{\pi}} \cdot \frac{A}{b^{3/2}} \cdot \frac{Q^2}{cdK}. \quad \dots \dots \dots (19)$$

From this formula we can get an estimate of N . For this purpose we may take the polonium α -particle, which has energy $2.09 \cdot 10^{-13}$ cal. and a range of $7.03 \cdot 10^{-4}$ cm. in platinum. Then

$$Q = 2.98 \cdot 10^{-10} \text{ cal./cm.}$$

Taking for c, d , and K the ordinarily accepted values from the tables, we get

$$N = 2.12 \cdot 10^{-20} \frac{A}{b^{3/2}}.$$

Now the values of b and A vary very much with the conditions of the surface of the platinum. Taking the lowest and the highest value*, we get the following results :—

TABLE II.

	A.	C.	N.	Volt.
Richardson	7.5×10^{25}	4.43×10^4	0.15	2.5
„	5.0×10^{28}	6.8×10^4	59.0	3.5
Langmuir	2.02×10^{31}	8.0×10^4	19,000	4.1

In the first two columns are the values for A and b , and in the third the number of emitted electrons. We see that N will vary very much, from 0.15 to 19,000.

The actual values of N obtained from experiments on δ -radiation lie between the values given above, and, as has been shown by Pound† and Bumstead & McGougan‡,

* Value taken from Richardson, *loc. cit.* p. 81.

† Pound, *Phil. Mag.* xxiii. p. 813 (1912).

‡ Bumstead & McGougan, *Phil. Mag.* xxiv. p. 462 (1912).

depend very much on the conditions of the surface, and vary in the same way as the thermionic radiation; for instance, the presence of hydrogen occluded in the surface diminishes the δ -radiation as well as the thermionic emission. The conditions under which the experiments on δ -radiation were performed are similar to those in which Richardson obtained the values of A and b ; and here we have a numerical agreement with the theoretical results. The value for N obtained from Langmuir's data is enormous, but Langmuir worked in extremely high vacuum, in which no δ -ray experiments have been made. According to this theory we should expect also an increase in the δ -radiation when high-vacuum conditions are reached.

Other facts observed in connexion with δ -radiation phenomena may be explained by this theory. For instance, it has been observed that the source of α -rays itself emits many more electrons of the δ -radiation per α -particle than a plate which the α -particles hit after leaving the source. The explanation of this phenomenon may be as follows:—If the α -particle strikes the body at a small glancing angle, the electrons would be emitted from a larger surface because the cross section of the cylinder increases with decreasing glancing angle. Now there will be α -particles going back, at all glancing angles to the surface, into the metal plate which carries the radioactive substance, whereas all the α -particles which hit an external plate do so nearly at right angles to the surface. So we may expect more δ -radiation to come from the source itself than from an external plate. Also, if an α -particle is slipping on the surface of the source, then some of the ionized electrons which have velocities perpendicular to the path of the α -rays as well as to the surface could escape from the source at a speed which may be high. This explanation may account for the high-speed electrons observed from the sources by Bumstead and McGougan* and Wertenstein†.

The speed of the greater number of the δ -radiation electrons, according to the approximate measurements of Hauser‡, is less than 6 volts, and the distribution of speeds is Maxwellian. We can, from the formula (18), get an estimate of the most probable speed of the emitted electrons. For this purpose we have to find the temperature at which the largest number of electrons is emitted. This is by

* *Loc. cit.*

† *Le Radium*, ix. p. 6 (1912).

‡ *Physikalische Zeitschrift*, p. 936, 1912.

differentiating (18) thus :

$$\frac{d^3N}{dT^3} = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

which gives for T the value

$$T = \frac{2}{3} b.$$

The energy in volts of the emitted electrons which corresponds to this temperature is given in the fourth column of Table II., and lies between 2.5 and 4.1 volts. So again we see that the theory is in agreement with experiment.

From the above discussion we may assume that the radiation, in general, has the same origin as thermionic emission, the difference being that in the case of thermionic emission the energy is supplied to the electrons by heating, while in the case of δ -radiation the energy is supplied by the α -particle. The calculations made above are not rigid enough to enable us to get a very close numerical agreement between theory and practice, but are sufficient to show that the δ -radiation may be explained using the same constants as are used in the case of thermionic emission. The enormous influence of the conditions of the surface on the magnitude of both types of radiation makes a more detailed calculation useless.

The same method of calculation may be applied to the case of a positive ray or to a beam of electrons which, striking a solid surface, produces a secondary emission of slow electrons. In this case slow-moving particles strike a body, but they do not penetrate deep in the surface. The heat given up by the entering particle at the first instant must be considered as concentrated in a point and afterwards dissipated in the body perpendicularly to a spherical surface. The problem may be treated in the same way as the previous one, only using spherical co-ordinates instead of cylindrical ones.

The solution will be

$$T = \frac{Q'}{4\pi^{\frac{1}{2}}} \sqrt{\frac{cd}{K^{\frac{1}{2}}}} \cdot \frac{1}{\sqrt{t^{\frac{1}{2}}}} e^{-\frac{cd}{4K} \cdot \frac{r^2}{t}}, \quad . \quad . \quad . \quad (21)$$

where Q' is the total energy of the particle which enters the body.

Performing the integration as before, we find a more complicated expression for N :

$$N = \frac{A}{\sqrt[3]{32\pi}} \frac{Q'^{\frac{1}{2}}}{K \sqrt[3]{cd}} \int_0^{\infty} \frac{e^{-\frac{T}{b}}}{T^{11/6}} dT. \quad . \quad . \quad . \quad (22)$$

The most probable speed of the emergent electrons calculated in the same way as (20), (21) comes to

$$T = \frac{6}{11} b.$$

This means that the most probable energy of the emergent electrons will be 1.36 times the value found in the previous case. See (20).

If we consider electrons or positive rays with gradually increasing penetrative power, we proceed gradually from expression (22) to the expression (19). This means that for a certain depth of penetration the number of the emitted secondary electrons stops increasing. This is actually found to be the case experimentally.

I am indebted to Dr. E. V. Appleton for his kind assistance in the preparation of this paper.

Cavendish Laboratory,
Cambridge.

CI. *Tensors of given Types in Riemann Space.*

By PHILIP FRANKLIN*.

ONE method of arriving at the laws of nature which describe certain phenomena, which has been given prominence by the theory of relativity, consists in deciding on the degree of mathematical complexity required, writing down the most general expressions of this degree of complexity, and using some of the known characteristics of the phenomena to specialize or reduce in number the constants entering into this expression. If the result obtained explains the known experiments in the field under discussion, it is accepted as a physical law; if not expressions of greater complexity are tried†.

According to the theory of relativity, all physical laws are, in their mathematical expression, statements of the equality of tensors. Consequently it becomes of importance to determine what tensors of given types are possible, and the object of the present paper is to prove a series of theorems useful in this connexion. A few examples of their application are added.

* Communicated by the Author. Presented to the American Mathematical Society, Dec. 27, 1922.

† The point of view here adopted, while in the main that of most writers on relativity, is in the precise form given the outcome of a series of discussions in the Seminar of Professors L. P. Eisenhart and O. Veblen at Princeton University.

We shall first consider tensors in Euclidean space, referred to Cartesian coordinates. That is, the transformations admitted are linear orthogonal ones, which leave the bilinear form

$$\delta_{ab}x^ay^b \dots \dots \dots (1)$$

(δ_{ab} equals 1 or 0 according as a is or is not equal to b) invariant. If we define an *arithmetic* tensor as one whose components are constant, being independent of both the position of the point and the particular set of Cartesian coordinates used; then we have:—

THEOREM I. *There are no non-vanishing arithmetic tensors of odd order; every arithmetic tensor of even order ($2p$) may be expressed as a linear combination of products of p tensors of type (1).*

Proof. Consider the arithmetic tensor

$$A_{abc\dots}x^ay^bz^c\dots \dots \dots (2)$$

For the special choice of vectors $x^i = \delta_{1i}$, $y^i = \delta_{2i}$, $z^i = \delta_{3i}$ (i from 1 to n , the dimensionality of the space), its value is

$$A_{123\dots} \dots \dots \dots (3)$$

If the index 1 appears an *odd* number of times in this term, then on using new coordinates which only differ from the old in having the direction of the 1-axis reversed, our vectors will have the same components as before except that x^1 (and any other non-zero 1-component) will have its sign changed. Consequently the value of the tensor for this choice of coordinates will be

$$-A_{123\dots} \dots \dots \dots (4)$$

and since the value of a tensor is independent of the coordinates, we must have this term equal to 0. By a similar argument, we may show that any component of a tensor which involves any index an odd number of times must be zero. Since every component of a tensor of odd order must contain at least one index an odd number of times, if such a tensor is arithmetic, all of its components must be zero, which is the first part of our theorem.

For tensors of even order, we shall only state the proof in detail for the case of sixth order tensors; the method is, however, general. If our tensor is

$$A_{abcdef}x^ay^bz^cu^dv^ew^f \dots \dots \dots (5)$$

for the special choice of vectors $x^i = y^i = \delta_{1i}$; $z^i = u^i = \delta_{2i}$; $v^i = w^i = \delta_{3i}$, its value is

$$A_{112233}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

while if we interchange the 1- and 2-axes, its value for the same vectors is

$$A_{221133}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Consequently these terms must be equal, and in general we have the result that any two components of our tensors which may be obtained from one another by a transposition (and hence by any substitution) of their subscripts must be equal.

It follows from this that if we subtract the expression

$$\delta_{ab} \delta_{cd} \delta_{ef} A_{112233} x^a y^b z^c u^d v^e w^f \dots, \quad . \quad . \quad . \quad (8)$$

where the dots stand for the similar terms formed from the 14 other components distinct from each other and from A_{112233} , which is a tensor because of its relation to (1), from the tensor (5), the result

$$B_{abcdef} x^a y^b z^c u^d v^e w^f \quad . \quad . \quad . \quad . \quad (9)$$

will be an arithmetic tensor with all terms containing any index an odd number of times, as well as those containing three distinct indices, zero. If we prove that this tensor has all its terms zero, we shall have proved our theorem.

The value of the tensor (9) is zero for the special choice of vectors $x^i = y^i = \delta_{1i}$; $z^i = u^i = \delta_{2i}$; $v^i = w^i = \delta_{3i}$; used above. If we now take as axes a set differing from the first in having those in the 1-2 plane rotated through half a right angle, these vectors will have as components:

$$x = y = \left(\sqrt{\frac{1}{2}} \quad \sqrt{\frac{1}{2}} \quad 0 \quad 0 \dots \right),$$

$$z = u = \left(-\sqrt{\frac{1}{2}} \quad \sqrt{\frac{1}{2}} \quad 0 \quad 0 \dots \right),$$

$$v = w = \left(0 \quad 0 \quad 1 \quad 0 \dots \right),$$

and the value of the tensor will be

$$\frac{1}{4} B_{111133} + \frac{1}{4} B_{222233} = -\frac{1}{2} B_{111133}, \quad . \quad . \quad . \quad (10)$$

Therefore this term and similarly all the terms involving two distinct indices are zero.

Finally if we take

$$x = y = z = u = (1 \quad 0 \quad 0 \quad 0 \dots),$$

$$v = w = (0 \quad 1 \quad 0 \quad 0 \dots),$$

the tensor has the value zero ; while on rotating the axes as before, the components are

$$\begin{aligned}x=y=z=u&=(\sqrt{\frac{1}{2}} \quad \sqrt{\frac{1}{2}} \quad 0 \quad 0 \dots), \\v=w&=(-\sqrt{\frac{1}{2}} \quad \sqrt{\frac{1}{2}} \quad 0 \quad 0 \dots),\end{aligned}$$

and its value is

$$\frac{1}{8} B_{11111} + \frac{1}{8} B_{22222} = \frac{1}{4} B_{11111}, \quad \dots \quad (11)$$

which shows that all the B's are zero, and completes the proof.

THEOREM II. *If a set of numerical constants has the property that the linear functions of the components of any tensor of the n th order with these as coefficients are the components of a tensor of the m th order, then these numerical constants are the components of two arithmetic tensors of the $m+n$ th and m th orders respectively; the tensor of the m th order is formed by multiplying the tensor of the n th order by the arithmetic tensor of the $m+n$ th order, contracting with respect to its n indices, and adding the arithmetic tensor of the m th order.*

We state the proof for the case $m=n=2$. If Q_{ab} is the tensor of the m th order to be formed, and A_{cd} is the arbitrary tensor of the n th order, we may write

$$Q_{ab} = p_{abcd} A_{cd} + q_{ab}, \quad \dots \quad (12)$$

where the p 's and q 's are the numerical constants. Since A is an arbitrary tensor, we may take it as identically zero, which shows that the q_{ab} are the components of a tensor, necessarily arithmetic. Therefore

$$Q_{ab} - q_{ab} = P_{ab} = p_{abcd} A_{cd} \quad \dots \quad (13)$$

is a tensor. If we replace the arbitrary A_{cd} in this last equation by the product of two vectors, and multiply both members by the product of two new arbitrary vectors, we obtain :

$$P_{ab} u^a v^b = p_{abcd} x^c y^d u^a v^b. \quad \dots \quad (14)$$

The left member of this equation is an invariant, and since the right member is the product of p_{abcd} by four arbitrary vectors, it follows that the p 's are transformed like the components of a tensor of the fourth order, and since they are constant, they must be the components of an arithmetic tensor.

As an application of this theorem, we consider the expressions for the stresses in a viscous fluid. We assume

that the terms in the stress tensor due to the viscosity depend linearly on the special derivatives of the velocity $\partial u_c / \partial x_d$ (which are the components of a tensor of the second order since the velocity u_c is a vector); and that the terms in these derivatives vanish for a symmetric dilatation, i. e. in case $\partial u_c / \partial x_d = k \delta_{cd}$.

Since the stress tensor is of the second order, by theorems I. and II. it must be of the form :

$$S_{ab} = A \delta_{ab} + (B \delta_{ab} \delta_{cd} + C \delta_{ac} \delta_{bd} + D \delta_{ad} \delta_{bc}) \partial u_c / \partial x_d. \quad (15)$$

Since S_{ab} must be symmetric in a and b , we have $C = D$, and our condition about the vanishing of the last terms for a dilatation gives :

$$3B + C + D = 3B + 2C = 0. \quad (16)$$

This shows that

$$S_{ab} = A \delta_{ab} + C \{ (\partial u_a / \partial x_b + \partial u_b / \partial x_a) - \frac{2}{3} \Sigma_c \partial u_c / \partial x_c \delta_{ab} \}, \quad (17)$$

the ordinary expression where A is the pressure in the absence of friction, and C is the negative of the coefficient of viscosity. The above is a modified form of the derivation given by Einstein in his Princeton Lectures *.

In setting up the equations of gravitation and other equations in the general theory of relativity, we are led to form invariants and tensors which, from the analogous expressions in the Newtonian theory, we expect to be linear in the second derivatives of the components of the fundamental quadratic tensor (g_{ij}) as these components correspond to the Newtonian potential. This gives importance to the following theorems, which deal with the most general forms for tensors of given orders in Riemann space, linear in these second derivatives.

As these tensors are all found to depend on the curvature tensor, we shall collect here a few of the fundamental expressions related to it. In terms of the Christoffel symbols:

$$\Gamma_{bc}^a = \frac{1}{2} g^{as} \left(\frac{\partial g_{cs}}{\partial x_b} + \frac{\partial g_{bs}}{\partial x_c} - \frac{\partial g_{bc}}{\partial x_s} \right), \quad (18)$$

not themselves tensors, we define the following expressions, which may be proved to be tensors :

$$R_{bcd}^a = \left(\frac{\partial \Gamma_{bd}^a}{\partial x_c} - \frac{\partial \Gamma_{bc}^a}{\partial x_d} \right) + (\Gamma_{rc}^a \Gamma_{bd}^r - \Gamma_{rd}^a \Gamma_{bc}^r), \quad (19)$$

$$R_{bc} = R_{bca}^a, \quad (20)$$

$$R = g^{bc} R_{bc}. \quad (21)$$

* A. Einstein, 'The Meaning of Relativity,' Princeton, 1923, p. 22.

For a "geodesic coordinate system at a point," i. e. one in which, at the point in question, $g_{ij} = \delta_{ij}$, $\partial g_{ij} / \partial x_k = 0$, we have :

$$R_{bcd}^a = \frac{1}{2} \left(\frac{\partial^2 g_{bc}}{\partial x_a \partial x_d} + \frac{\partial^2 g_{ad}}{\partial x_b \partial x_c} - \frac{\partial^2 g_{ac}}{\partial x_b \partial x_d} - \frac{\partial^2 g_{bd}}{\partial x_a \partial x_c} \right), \quad (22)$$

$$R_{bc} = \frac{1}{2} \left(\frac{\partial^2 g_{bc}}{\partial x_a \partial x_a} + \frac{\partial^2 g_{aa}}{\partial x_b \partial x_c} - \frac{\partial^2 g_{ac}}{\partial x_a \partial x_b} - \frac{\partial^2 g_{ab}}{\partial x_a \partial x_c} \right), \quad (23)$$

$$R = \frac{\partial^2 g_{bb}}{\partial x_a \partial x_a} - \frac{\partial^2 g_{ab}}{\partial x_a \partial x_b}, \quad (24)$$

at the origin of the geodesic coordinate system.

Concerning invariants in Riemann space, we have :

THEOREM III. *The most general invariant involving the g_{ij} 's, together with their first and second derivatives, and these last linearly, is a linear function of the Riemann scalar curvature, R ; i. e., $AR + a$, where A and a are constants*.*

By hypothesis, the invariant sought must be of the form :

$$I = U + V_{ab,cd} \frac{\partial^2 g_{ab}}{\partial x_c \partial x_d}, \quad (25)$$

where U and the V 's are functions of the g_{ij} and of their first derivatives. From the symmetry of the g_{ij} and of their second derivatives it follows that the $V_{ab,cd}$ may be taken to be symmetric in the pairs of indices ab and cd without real loss of generality.

If, at a point in our space, we introduce a geodesic coordinate system, we shall have

$$g_{ij} = \delta_{ij}, \quad \partial g_{ij} / \partial x_k = 0, \quad (26)$$

at the point, and (25) becomes

$$I = a + b_{ab,cd} \frac{\partial^2 g_{ab}}{\partial x_c \partial x_d}, \quad (27)$$

where the b 's and a are now constants, independent of the point selected. (27) must be an invariant under all transformations which do not disturb the conditions (26). But, for a linear orthogonal transformation we have :

$$\left. \begin{aligned} x_i &= p_{ij} \bar{x}_j \quad \text{where} \quad \delta_{ab} p_{ai} p_{bk} = \delta_{ik}, \\ \bar{g}_{ik} &= g_{ab} p_{ai} p_{bk} \quad \text{since} \quad \bar{g}_{ik} \bar{x}_i \bar{x}_k = g_{ab} x_a x_b, \\ \partial \bar{g}_{ik} / \partial \bar{x}_r &= \partial g_{ab} / \partial x_c p_{ai} p_{bk} p_{cr}, \end{aligned} \right\} . . . (28)$$

and hence such transformations do leave (26) invariant.

* The proof here given was suggested by that of H. Weyl, see his *Raum, Zeit, Materie*, fourth edition, p. 287.

But since, for such transformations, we also have

$$\partial^2 \bar{g}_{ik} / \partial x_r \partial x_s = \partial^2 g_{ab} / \partial x_c \partial x_d p_{ai} p_{bk} p_{cr} p_{ds}, \quad (29)$$

the second derivatives in (27) are transformed like the components of a tensor, and hence the b 's must be the components of an arithmetic tensor (Theorem II.), and by Theorem I. we must have

$$b_{ab,cd} = A \delta_{ab} \delta_{cd} + B \delta_{ac} \delta_{bd} + C \delta_{ad} \delta_{bc}. \quad (30)$$

The conditions of symmetry make $B=C$, giving :

$$b_{ab,cd} = A \delta_{ab} \delta_{cd} + B(\delta_{ac} \delta_{bd} + \delta_{ad} \delta_{bc}). \quad (31)$$

But (26) also remains true if we subject the coordinates to the transformation

$$x_a = \bar{x}_a + \frac{1}{6} P_{a,bcd} \bar{x}_b \bar{x}_c \bar{x}_d, \quad (32)$$

where the P 's are an arbitrary set of constants, symmetrical in b, c , and d ; for this gives :

$$\left. \begin{aligned} \partial x_a / \partial \bar{x}_i &= \delta_{ai} + \frac{1}{2} P_{a,icd} \bar{x}_c \bar{x}_d, \\ \bar{g}_{ik} &= \partial x_a / \partial \bar{x}_i \partial x_b / \partial \bar{x}_k g_{ab} \\ &= (\delta_{ai} + \frac{1}{2} P_{a,icd} \bar{x}_c \bar{x}_d) (\delta_{bk} + \frac{1}{2} P_{b,kcd} \bar{x}_c \bar{x}_d) g_{ab}. \end{aligned} \right\} \quad (33)$$

For the transformation (32), we also have, for the origin,

$$\partial^2 g_{ab} / \partial \bar{x}_c \partial \bar{x}_d = \partial^2 g_{ab} / \partial x_c \partial x_d + P_{a,bcd} + P_{b,acd}, \quad (34)$$

as is easily seen from (33). Therefore, since (27) remains invariant under such transformations, we must have

$$b_{ab,cd} (P_{a,bcd} + P_{b,acd}) = 2b_{ab,cd} P_{a,bcd} = 0. \quad (35)$$

In particular, if we take $P_{a,bcd} = \delta_{a1} \delta_{b1} \delta_{c1} \delta_{d1}$, and combine (31) and (35), we obtain

$$A + 2B = 0; \quad B = -\frac{1}{2}A. \quad (36)$$

Therefore (27) can be written

$$I = A(\partial^2 g_{aa} / \partial x_b \partial x_b - \partial^2 g_{ab} / \partial x_a \partial x_b) + a, \quad (37)$$

or in virtue of (24)

$$I = AR + a. \quad (38)$$

Hence our invariant can be put in this form at any point for the special coordinates chosen, and since this is known to be an invariant for constant values of A and a , it is so expressible in any coordinates.

THEOREM IV. *The most general covariant tensor of the second order involving the g_{ij} 's, together with their first and*

second derivatives, and these last linearly, is a linear combination of R_{ik} , Rg_{ik} , and g_{ik} .*

We have by hypothesis :

$$T_{gh} = U_{gh} + V_{gh, ab, cd} \partial^2 g_{ab} / \partial x_c \partial x_d, \quad \dots \quad (39)$$

where the U 's and V 's are functions of the g 's and their first derivatives, and the latter are symmetric in the pairs of indices ab and cd . As before, on introducing a geodesic coordinate system, we have for the origin :

$$T_{gh} = a_{gh} + b_{gh, ab, cd} \partial^2 g_{ab} / \partial x_c \partial x_d \quad \dots \quad (40)$$

As this must be a tensor for linear orthogonal transformations, and for such transformations (29) holds, we have by theorem II. that a_{gh} is an arithmetic tensor of the second order (δ_{gh}) and $b_{gh, ab, cd}$ is one of the sixth order. Hence by theorem I. we must have, in view of the symmetry :

$$\left. \begin{aligned} b_{gh, ab, cd} = & A(\delta_{gh} \delta_{ab} \delta_{cd}) + B(\delta_{gh} \delta_{ac} \delta_{bd} + \delta_{gh} \delta_{ad} \delta_{bc}) \\ & + C(\delta_{ab} \delta_{cg} \delta_{dh} + \delta_{ab} \delta_{ch} \delta_{dg}) + D(\delta_{cd} \delta_{ag} \delta_{bh} + \delta_{cd} \delta_{ah} \delta_{bg}) \\ & + E(\delta_{ag} \delta_{bc} \delta_{hd} + \delta_{bg} \delta_{ac} \delta_{hd} + \delta_{ag} \delta_{bd} \delta_{hc} + \delta_{bg} \delta_{ad} \delta_{hc}) \\ & + F(\delta_{ah} \delta_{bc} \delta_{gd} + \delta_{bh} \delta_{ac} \delta_{gd} + \delta_{ah} \delta_{bd} \delta_{gc} + \delta_{bh} \delta_{ad} \delta_{gc}). \end{aligned} \right\} \quad (41)$$

By using (32) and (34) in the same way as before, we find

$$b_{gh, ab, cd} P_{a, bcd} x^g y^h = 0, \quad \dots \quad (42)$$

since $T_{gh} x^g y^h$ is an invariant, and (32) leaves the components of the arbitrary vectors x and y , situated at the origin, unchanged. As the P 's in (42) are arbitrary, except for their symmetry in b , c , and d , we may obtain various relations between the constants in (41) by taking special values. Taking $x^i = y^i = \delta_{2i}$, $P_{a, bcd} = \delta_{a1} \delta_{b1} \delta_{c1} \delta_{d1}$ gives :

$$A + 2B = 0; \quad \dots \quad (43)$$

$x^i = y^i = \delta_{1i}$, $P_{a, bcd} = \delta_{a1} \delta_{b1} \delta_{c1} \delta_{d1}$ gives

$$A + 2B + 2C + 2D + 4E + 4F = 0; \quad \dots \quad (44)$$

$x^i = \delta_{2i}$, $y^i = \delta_{1i}$, $P_{a, bcd} = \delta_{a2} \delta_{b1} \delta_{c1} \delta_{d1}$ gives :

$$D + 2E = 0; \quad \dots \quad (45)$$

and finally $x^i = \delta_{1i}$, $y^i = \delta_{2i}$, $P_{a, bcd} = \delta_{a2} \delta_{b1} \delta_{c1} \delta_{d1}$ gives :

$$D + 2F = 0. \quad \dots \quad (46)$$

* This theorem is stated by Weyl (*loc. cit.*). The theorem is discussed by M. v. Laue, *Die Relativitätstheorie* (1921 edition, vol. ii. p. 100f.) He fails to consider the term g_{ik} , which is independent of the second derivatives.

It follows from the last four equations that

$$A = -2B; C = D = -2E = -2F. \quad . \quad . \quad (47)$$

This shows that (40) may be written :

$$\left. \begin{aligned} T_{gh} = & \delta_{gh} \Lambda (\partial^2 g_{aa} / \partial x_b \partial x_b - \partial^2 g_{ab} / \partial x_a \partial x_b) \\ & + C (\partial^2 g_{gh} / \partial x_a \partial x_a + \partial^2 g_{aa} / \partial x_g \partial x_h - \partial^2 g_{ah} / \partial x_a \partial x_g \\ & - \partial^2 g_{ag} / \partial x_a \partial x_h) + K \delta_{gh}. \end{aligned} \right\} \quad (48)$$

But, according to (23) and (24) this is the value of

$$T_{gh} = A R g_{gh} + 2 C R_{gh} + K g_{gh} \quad . \quad . \quad (49)$$

in the coordinates chosen. Since g_{gh} and R_{gh} are known to be covariant tensors, this must represent the tensor T in any coordinates, and the theorem is proved.

By the aid of theorem IV. we may easily arrive at Einstein's law of gravitation as the generalization of Poisson's equation for the Newtonian theory :

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} + \frac{\partial^2 \phi}{\partial z^2} = 4\pi k \rho. \quad . \quad . \quad (50)$$

In the generalization, we will replace the density of matter ρ by the energy tensor T_{gh} ; consequently for the left member we seek a tensor of the second order in the coefficients of the fundamental quadratic tensor (g_{ij}) which take the place of the single potential ϕ , and their derivatives. By analogy with (50) we expect the tensor to be linear in the second derivatives, and hence by theorem IV. our equation must be of the form (49) or

$$R_{gh} + s R g_{gh} + t g_{gh} = k T_{gh} \quad . \quad . \quad . \quad (51)$$

after a change of constants. Since it is known that the divergence of the tensor T_{gh} vanishes ($\partial T_{gh} / \partial x_h = 0$, in geodesic coordinates) this must be true for the left member of (51). But its divergence (in geodesic coordinates) is

$$(\frac{1}{2} + s) (\partial^3 g_{aa} / \partial x_b \partial x_b \partial x_g - \partial^3 g_{ab} / \partial x_a \partial x_b \partial x_g), \quad (52)$$

as is seen from (23) and (24). This shows $s = -\frac{1}{2}$. To interpret the meaning of t , we multiply (51) by g^{gh} and sum for both indices. We thus obtain

$$\left. \begin{aligned} R + 4s R + 4t &= k T_{gh} g^{gh}, \\ \text{or} \quad 4t - R &= k T_{gh} g^{gh}. \end{aligned} \right\} \quad . \quad . \quad . \quad (53)$$

Hence, at points for which $T_{gh} = 0$, R has the constant value $4t$, and if we call this value R_0 , (51) may now be written :

$$R_{gh} - \frac{1}{2} R g_{gh} + \frac{1}{4} R_0 g_{gh} = k T_{gh}. \quad . \quad . \quad (54)$$

In his earlier papers Einstein assumed $R_0=0$, later* he considered the general case. The derivation of (54) just given is similar to that given by Einstein in his Princeton Lectures †.

THEOREM V. *The most general tensor of the fourth order involving the g_{ij} 's together with their first and second derivatives and these last linearly has as its covariant components a linear combination of R_{efgh} ($g_{es}R_{fgh}^s$), $g_{ef}R_{gh}$, $g_{ef}g_{gh}R$, $g_{ef}g_{gh}$ and the terms which can be formed from them by permuting the indices.*

We assume our tensor is

$$T_{efgh} = U_{efgh} + V_{efgh, ab, cd} \partial^2 g_{ab} / \partial x_c \partial x_d, \quad \dots \quad (55)$$

and as before consider the form in geodesic coordinates :

$$T_{efgh} = a_{efgh} + b_{efgh, ab, cd} \partial^2 g_{ab} / \partial x_c \partial x_d, \quad \dots \quad (56)$$

By reasoning similar to that used for theorem IV. we show that a_{efgh} and $b_{efgh, ab, cd}$ are arithmetic tensors ; also that

$$b_{efgh, ab, cd} P_{a, bcd} x^e y^f z^g u^h = 0 \quad \dots \quad (57)$$

for an arbitrary choice of P's (symmetric in bcd), x , y , z , and u .

Consider the terms in $b_{efgh, ab, cd}$ which contain δ_{ef} , and write them collectively as $\delta_{ef} q_{gh, ab, cd}$. If we take $x^i = y^i = \delta_{i3}$, $z^3 = u^3 = 0$, and give the P's such values that they are zero if a , b , c , or d are 3, the only non-zero terms in (57) will be

$$q_{gh, ab, cd} P_{a, bcd} z^g u^h = 0. \quad \dots \quad (58)$$

We may apply to this equation the same argument we used on (42) above, as the q here is an arithmetic tensor with the same symmetry properties as the b of (42), and our restriction on the zero components when the indices are three is consistent with the values there used. Thus we may show the part of (55) resulting from $\delta_{ef} q_{gh, ab, cd}$ is of the form (cf. (49)) :

$$A g_{ef} g_{gh} R + C g_{ef} R_{gh} + K g_{ef} g_{gh}, \quad \dots \quad (59)$$

and a similar argument would apply to the terms involving a δ which contained both indices from the four $e f g h$. Thus the sum of all such terms corresponds to a part of (55) which is a tensor, and from now on we may confine our

* A. Einstein, "Kosmologische Betrachtungen zur allgemeinen Relativitätstheorie," *Sitzungsber. der Preuss. Akad. d. Wiss.* 1917, p. 142.

† L. c. p. 92.

remarks to the tensor left when this is subtracted from our original tensor. The corresponding part of b contains the following terms, where the coefficients are equal as indicated because of the symmetry :—

$$\left. \begin{aligned} & G(\delta_{ae}\delta_{hf}\delta_{cg}\delta_{dh} + \delta_{af}\delta_{hg}\delta_{ce}\delta_{dh} + \delta_{ae}\delta_{bf}\delta_{ch}\delta_{dg} + \delta_{af}\delta_{be}\delta_{ch}\delta_{dg}) \\ & + H(\delta_{ag}\delta_{bh}\delta_{ce}\delta_{df} + \delta_{ah}\delta_{bg}\delta_{ce}\delta_{df} + \delta_{ag}\delta_{bh}\delta_{cf}\delta_{de} + \delta_{ah}\delta_{bg}\delta_{cf}\delta_{de}) \\ & + I(\delta_{af}\delta_{hg}\delta_{ce}\delta_{dh} + \delta_{ag}\delta_{hf}\delta_{ce}\delta_{dh} + \delta_{af}\delta_{bg}\delta_{ch}\delta_{de} + \delta_{ag}\delta_{bf}\delta_{ch}\delta_{de}) \\ & + J(\delta_{ae}\delta_{bh}\delta_{cf}\delta_{dg} + \delta_{ah}\delta_{be}\delta_{cf}\delta_{dg} + \delta_{ae}\delta_{bh}\delta_{cg}\delta_{df} + \delta_{ah}\delta_{be}\delta_{cg}\delta_{df}) \\ & + K(\delta_{af}\delta_{bh}\delta_{ce}\delta_{dg} + \delta_{ah}\delta_{bf}\delta_{ce}\delta_{dg} + \delta_{af}\delta_{bh}\delta_{cg}\delta_{de} + \delta_{ah}\delta_{bf}\delta_{cg}\delta_{de}) \\ & + L(\delta_{ae}\delta_{hg}\delta_{cf}\delta_{dh} + \delta_{ag}\delta_{be}\delta_{cf}\delta_{dh} + \delta_{ae}\delta_{bg}\delta_{ch}\delta_{df} + \delta_{ag}\delta_{be}\delta_{ch}\delta_{df}). \end{aligned} \right\} \quad (60)$$

For this part alone we still have (57). If we take $x^i = \delta_{i2}$, $y^i = z^i = u^i = \delta_{i1}$ and $P_{a,bcd} = \delta_{a2}\delta_{b1}\delta_{c1}\delta_{d1}$, we obtain by combining (60) with (57):

$$G + J + L = 0. \quad . \quad . \quad . \quad . \quad . \quad (61)$$

For $y^i = \delta_{i2}$, $x^i = z^i = u^i = \delta_{i1}$ and $P_{a,bcd} = \delta_{a2}\delta_{b1}\delta_{c1}\delta_{d1}$,

$$G + I + K = 0, \quad . \quad . \quad . \quad . \quad . \quad (62)$$

and by taking in turn $z^i = \delta_{i2}$ and $u^i = \delta_{i2}$ we obtain similarly:

$$\left. \begin{aligned} & H + I + L = 0, \\ & H + J + K = 0 \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad . \quad (63)$$

These equations show that

$$G = H; \quad I = J; \quad K = L = -G - I, \quad . \quad . \quad (64)$$

and consequently the part of (56) corresponding to (60) is

$$\left. \begin{aligned} & g(G(\partial^2 g_{ef}/\partial x_g \partial x_h + \partial^2 g_{gh}/\partial x_e \partial x_f \\ & \quad - \partial^2 g_{fh}/\partial x_e \partial x_g - \partial^2 g_{eg}/\partial x_f \partial x_h) \\ & + I(\partial^2 g_{gf}/\partial x_e \partial x_h + \partial^2 g_{eh}/\partial x_g \partial x_f \\ & \quad - \partial^2 g_{fh}/\partial x_e \partial x_g - \partial^2 g_{eg}/\partial x_f \partial x_h) \end{aligned} \right\}. \quad (65)$$

Comparison with (22) shows that this expression may be written

$$\text{or} \quad \left. \begin{aligned} & G R^h_{efg} + I R^h_{gfe} \\ & G g_{hx} R^x_{efg} + I g_{hx} R^x_{gfe} \end{aligned} \right\}, \quad . \quad . \quad . \quad . \quad (66)$$

as in the normal coordinate system the g 's are replaced by δ 's, and the second form is used since we are considering the covariant components of our tensor. (59) and (66) show

that our tensor may be written, with a change of notation for the constants :

$$\left. \begin{aligned} & AR_{hfg} + BR_{hgf} + Cg_{ef}R_{gh} + Dg_{gh}R_{ef} \\ & + Eg_{eg}R_{fh} + Fg_{fh}R_{eg} + Gg_{eh}R_{fg} + Hg_{fg}R_{eh} \\ & + Ig_{ef}g_{gh}R + Jg_{eg}g_{fh}R + Kg_{eh}g_{fg}R \\ & + Lg_{ef}g_{gh} + Mg_{eg}g_{fh} + Ng_{eh}g_{fg} \end{aligned} \right\}. \quad (67)$$

The tensor we have found may also be described as a linear combination of all the tensors of the fourth order which can be obtained by multiplying the curvature tensor R^e_{fgh} (or a scalar) by the fundamental quadratic tensor (g_{ij}) any number of times, and contracting to make the final order four. The tensors of this type not appearing explicitly in (67) are linearly dependent on those present in virtue of the relations :

$$R^e_{fgh} + R^g_{fhe} + R^h_{feg} = 0, \quad R_{ab} = R_{ba}, \text{ etc., } \dots \quad (68)$$

which follow from (22).

We conclude with the following generalization of the preceding three theorems, which includes them as special cases :—

THEOREM VI. *The most general tensor of given even order involving the g_{ij} 's and their first and second derivatives, these last linearly, is a linear combination of tensors which may be formed from the tensor R^e_{fgh} and the fundamental quadratic tensor (g_{ij}) by multiplication and contraction. There are no tensors of odd order of the type required.*

For the method used to separate out the terms in (59) above, may evidently be used to separate out all the terms for a tensor of order greater than four, and to reduce them to products of the fundamental quadratic tensor by those of the next lower even order. The last statement in the theorem follows from the non-existence of arithmetic tensors of odd order.

Theorems V. and VI. are believed to be new. They show that the complete theory of tensors of the type discussed depends on the curvature tensor R^e_{fgh} which plays the same role for these tensors that the fundamental quadratic tensor does for arithmetic tensors. The theorems are presented here not only for their mathematical interest, but because of their possible use in physical applications.

Harvard University.
Sept. 1922.

CII. *Directional Observations of Atmospherics—1916–1920.*

*By R. A. WATSON WATT, B.Sc., F. Inst. P.**

[Published by permission of the Radio Research Board.]

I. *Source of Data.*

IN connexion with a Meteorological Office investigation into the Location of Thunderstorms by Radiotelegraphic Direction Finding, begun in 1915, Capt. C. J. P. Cave, R.E., then Meteorologist-in-charge at South Farnborough, was able to arrange, through the good offices of Captain Slee, R.N., that the coastal direction-finding stations of the Admiralty should supply reports of observations made, when the exigencies of the service permitted, on the strength and apparent direction of arrival of atmospherics. The purpose of this paper is to present the results of a statistical reduction of some of the data so obtained. Of twelve reporting stations, six were selected as having supplied data nearly continuously over a four-year period, these stations were:—

	Latitude.	Longitude.
Carnsore	52° 11' 50" N.	6° 21' 0" W.
Browhead	51° 27' 20" N.	9° 45' 30" W.
Lizard	49° 58' 55" N.	5° 12' 15" W.
Prawle	50° 13' 10" N.	3° 42' 40" W.
Flamborough	54° 07' 05" N.	0° 04' 55" W.
Peterhead	57° 33' 20" N.	1° 48' 55" W.

It will be noted that the stations form a fairly well extended network from S. Ireland to N.E. Scotland. The wave-length on which the observations were made was always short, and may be taken to be, on the average, some 400 metres.

The intensity of disturbance was reported on an arbitrary scale, it is not, however, proposed to discuss here anything other than the observed bearing, or apparent direction of arrival, of atmospherics. This was determined by the ordinary direction-finding method of estimation of relative signal strengths as the search-coil of a Bellini-Tosi radio-goniometer was rotated. The personnel of these stations developed amazing powers of aural discrimination in the application of this method, and the consistency of the data to be presented in the course of this report is a striking proof of their high skill applied to a peculiarly difficult and confusing type of direction finding. The variation of

* Communicated by the Author.

personnel from watch to watch, and transfers between stations, are believed to have nearly neutralized personal error as affecting comparison of observations from different periods and stations.

II. *Distribution of Data.*

Reporting began in March 1916, and the observations between that date and July 1920 are dealt with in this paper. The total number of observations discussed amounts to 12,973. Table 0 shows the distribution of these observations amongst stations and periods. For purposes of reduction the data have been grouped according to three-month seasons approximately centering on equinox or solstice, and according to a diurnal subdivision of four periods, morning, forenoon, afternoon, and evening. These periods were again grouped into "light" and "dark," and into "A.M." and "P.M." pairs. This classification was rendered necessary by the fact that observations were not made at fixed hours, but at any hour when atmospheric were prominent and when work permitted. Further, no observations were made between 2100 and 0400 G.M.T.

The result of these limitations, combined with the known higher intensity of atmospheric disturbance during the hours of darkness, is that a great majority of all observations fell close to the hours of 0600 and 2000 G.M.T.

III. *Most Frequent and Mean Directions of Maximum Disturbance.*

Frequency curves, showing the number of occasions on which a given azimuth from true North was reported as most disturbed, have been plotted for each station, for each of the subdivisions as to season, time of day, and illumination already mentioned. Typical curves are shown in fig. 1.

The directions forming the peaks of these frequency curves are tabulated as X_F in the summary of results, Table 1. They will be reviewed in some detail at a later point in this paper.

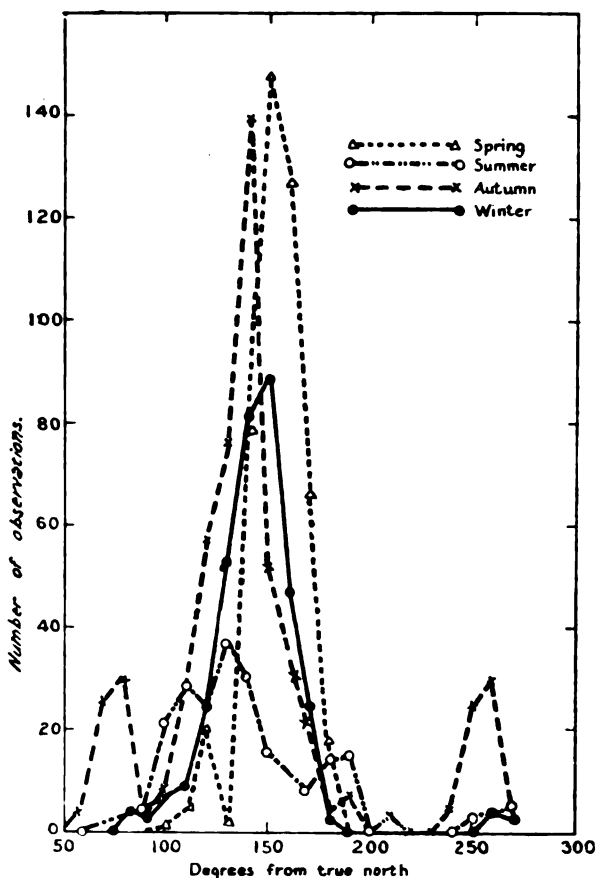
The whole of the observations are affected by the radio-goniometric ambiguity of 180° , since the direction-finder determines the vectorial direction without discrimination of sense. Thus an observation reported as 150° E. of N. may apply to disturbance originating $150^\circ + 180^\circ = 330^\circ$ E. of N. Actually this ambiguity is of small moment since, as mentioned in a previous communication*, all available

* "Directional Observations of Atmospheric, 1920-1921," Roy. Soc. Proc. A. 102, pp. 460-478 (1922).

evidence, both theoretical and observational, points to an overwhelming preponderance of origins in lower latitudes, *i.e.* of directions of arrival lying between 90° and 270°

Fig. 1.

Seasonal Frequency Curves. Flamborough.



(through 180°) E. of N. The present data in themselves support this interpretation, since simultaneous bearings taken at different stations almost invariably converge towards the South.

For statistical purposes, however, it has been considered that the most probable resolution of the ambiguity, in the

mass, would be to assign to all observations a sense such that the frequency curve has a peak directed in general, towards S.E. rather than N.W., and covers a range of 90° on either side of the peak. Thus, the average value of X_F being 150° , the frequency curves will in general extend from 60° to 240° E. of N., and to a reported bearing of 30° would be assigned the value 210° in this curve.

Station	Total	midnight sunrise		sunrise noon		noon sunset		sunset midnight		midnight noon		noon midnight		Spring		Summer		Autumn		Winter	
		T	m	f	a	e	L	D	A	M	P	M	P	P	M	A	W	A	W	A	W
Peterhead	1366	412	84	240	630	329	1037	500	868	428	201	424	313								
Framborough	1249	394	102	293	760	196	1153	452	1053	485	241	495	348								
Carnaro	4294	1188	384	945	1512	1318	2591	1706	2533	1226	966	776	1331								
Brownhead	2675	760	223	519	1173	743	1932	983	1622	748	453	711	765								
Prawle	1589	288	61	282	938	341	1228	348	1192	300	144	516	608								
Lizard	1515	261	38	323	893	354	1151	308	1207	302	175	484	554								
	2973																				
Peterhead	157	159	140	143	153	141	156	159	153	160	139	150	150								
Framborough	146	157	133	122	147	120	142	155	143	153	133	138	147								
Carnaro	149	152	147	143	147	144	150	151	148	148	153	157	148								
Brownhead	139	159	132	137	139	137	139	159	158	158	94	133	140								
Prawle	153	168	173	95	182	95	153	168	152	153	93	127	157								
Lizard	148	163	95	92	148	90	150	168	148	148	89	122	146								
Peterhead	5140.6	158.910.9	529.41.35	138.111.7	5140.6	136.711.5	1541.0.5	56.311.0	148.10.7	6.410.5	14.811.5	143.911.1	156.811.0								
Framborough	461.240.6	151.540.6	132.345.9	126.5167.42	310.6	126.111.6	145.41.6	147.211.5	138.310.7	15440.6	17.711.2	170.211.1	142.210.6								
Carnaro	168.440.4	53.610.8	15.811.5	14.111.0	147.310.5	145.40.8	150.10.5	152.710.7	145.310.5	150.210.5	147.411.0	150.111.1	147.40.8								
Brownhead	159.740.6	117.311.4	29.013.0	126.011.0	137.110.6	128.011.3	143.710.7	154.811.3	163.706.6	141.510.5	117.312.3	132.611.2	142.811.2								
Prawle	110.511.0	153.512.4	171.916.2	101.312.6	145.810.0	101.512.5	152.710.9	177.411.0	137.710.8	156.111.2	104.611.3	124.111.4	158.811.2								
Lizard	140.510.8	63.712.3	101.917.7	105.512.1	141.310.6	59.21.2	145.01.6	161.112.2	137.310.8	150.111.0	103.013.3	118.611.4	142.511.3								
Peterhead	21.7	17.7	33.8	25.8	15.3	28.3	16.7	23.6	20.2	10.6	21.4	22.6	18.2								
Framborough	24.4	16.4	39.6	28.8	19.6	32.5	19.6	27.0	24.2	13.4	25.0	28.5	18.3								
Carnaro	27.9	30.0	30.1	30.3	22.3	30.6	26.7	29.0	26.1	18.7	31.5	29.1	31.2								
Brownhead	32.6	37.8	43.9	36.4	20.8	36.5	30.0	39.6	26.6	25.6	45.0	32.3	37.0								
Prawle	38.8	38.8	48.7	44.2	27.2	47.7	32.4	39.1	34.8	20.3	45.0	43.1	30.1								
Lizard	30.9	36.9	47.7	40.7	20.5	41.5	26.4	38.2	30.9	16.6	41.9	31.2	30.4								

The observations in each group having thus been assigned to the range $X_F + 90^\circ$ (or, actually, to the range $\pm 90^\circ$ from the 5° point nearest to X_F , this approximation being necessary to reduce the labour of computation) the mean direction of arrival of atmospherics has been computed for the group and tabulated as X_M . Since all the frequency curves are more or less skew, X_M does not coincide with X_F , and their difference is taken as a measure of the skewness.

It may be remarked that, while the most frequent or modal value X_F would doubtless be, in a perfect series of observations on a skew distribution, the most probable value of the variable sought for, yet psychological considerations would seem to point to the possibility of the mean value X_M bringing out the finer detail of variations. For it is the most frequent value that impresses itself on the memory of the actual observer, and predisposes him to assign to a dubious determination the value nearer to X_F , so that the curve becomes overweighted towards X_F ; the value of X_M , which emerges only after statistical reduction, while suffering

somewhat from this overweighting, is a more sensitive index of the true variation.

Along with each mean value is tabulated the standard error of the mean. The distribution not being normal, the "probable error" will not be equal to two-thirds of the standard error but the error in assuming that this is so, should it be preferred to think in terms of the "probable" error, will be small.

IV. *The Standard Deviations.*

The standard deviations from mode and mean have also been computed and those referred to the mode have been tabulated. In no case is the skewness sufficient to make these two deviations differ by any considerable amount. These standard deviations give a convenient (inverse) measure of the "peakiness" of the distribution curves, and their seasonal and diurnal variations are in themselves interesting on this account.

V. *Diurnal Variation.*

As has already been stated, the observations were not made at fixed hours. The diurnal variation has, accordingly, been examined by subdivision into four main groups:—*m* (morning) containing observations made between midnight and sunrise, *f* (forenoon) sunrise to noon, *a* (afternoon) noon to sunset, and *e* (evening) sunset to midnight. On the whole the observations are crowded at the boundaries between *m* and *f* and between *a* and *e*.

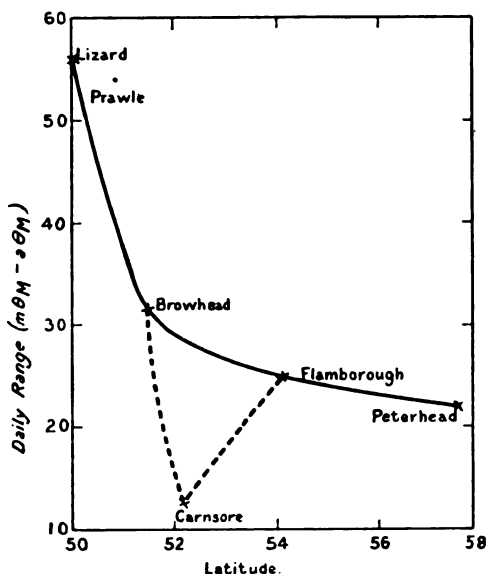
The unweighted mean of the most frequently disturbed directions for all six stations then varies from 160° in the morning, through 137° in the forenoon, to 122° afternoon, returning to 148° in the evening period. The use of mean values in place of modes does not appreciably alter these figures, which become 157° , 136° , 123° and 144° respectively. (It will, however, be noted that the skewness is greater during the dark hours.) There is, accordingly, a counter-clockwise swing of 34° range between morning and afternoon. The data from individual stations are as consistent as could be expected, the direction of swing being the same for all six in the periods *a* to *e* and *e* to *m*, slight swings opposite to those of the majority are shown by two stations in the period *f* to *a*, and by one in the period *m* to *f*. These irregularities are all within the range of probable error in the *f* and *a* groups, the "probable error" reaching 5° in some cases in *f*.

The diurnal range for each station may be specified by the quantity $(m\Theta_M - a\Theta_M)$, i.e., the difference between the mean values of the mean direction of arrival for the morning and afternoon groups. These quantities for the six stations are plotted in fig. 2, against the latitude of each station.

It will be seen that, excluding Carnsore, which shows, throughout the whole of the data, variations very much smaller than those at other stations, the range of diurnal variation decreases as the latitude increases.

Fig. 2.

Mean Daily Range of Mean Direction of Arrival of Atmospherics plotted against Latitude.

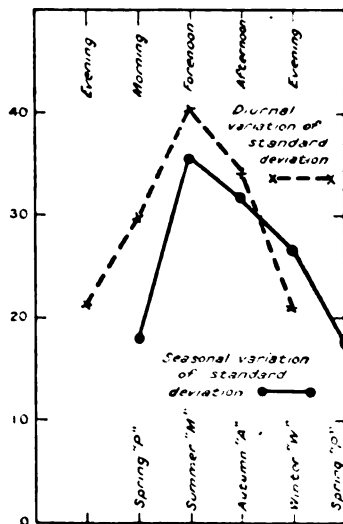


Proceeding from the range of variation in passing from one group to another, to the standard deviation, within the group, from the mode or mean for that group, we find a remarkable regularity in diurnal change. The standard deviation of the *f* group is, in five out of six cases (the exception being Carnsore), much higher than that of the *m* and *a* groups. In all cases the standard deviation of the *e* group is less than that of *f*, and also, for all stations except Flamborough, less than for the *m* group. Thus, with but slight exceptions, the standard deviation has a diurnal

variation of the type shown in fig. 3, which shows the unweighted means of standard deviations for all stations.

The standard deviations also show strongly the influence of latitude. Peterhead has the least standard deviation in each group, (save in one case where Flamborough is 1° lower) and the general run of each curve is that of increasing standard deviation with decreasing latitude till Prawle is reached, this station having the maximum standard deviation in three curves, its neighbour Browhead providing the fourth maximum. All four curves then show a sharp decrease in standard deviation as between Prawle and Lizard.

Fig. 3.



The grouping of the observations according to whether the sun was above or below the horizon at the time of observation shows that, on the mean of all stations, the apparent direction of arrival of atmospherics varies from 122° E. of N. in daylight to 148° in darkness. All six stations without exception show a shift in the same direction though of varying amount.

Similarly there is a difference of 13° between the mean modes of observations taken in the "A.M." period 0000 to 1200, and those in the "P.M." period 1200 to 2400, the "A.M." value being 160° , the "P.M." 147° . The means of the corresponding means are 159° and 141° . Again the

shift is in the same direction at all stations. The skewness of the "P.M." distribution is noteworthy.

The standard deviations in the "light" group are some 50 per cent. higher than in the "dark," those of the "A.M." group some 20 per cent. higher than those of the "P.M." group.

VI. *The Seasonal Variation.*

The seasonal variation in the unweighted mean of the modal values is from 150° in Spring (February, March, and April) to 118° in Summer, returning through 138° in Autumn and 148° in Winter. Using means in place of modes these figures become 152° , 125° , 136° , and 149° .

Measuring annual range, in a manner similar to that adopted for daily range, $P_M - M_M$, the difference between Spring and Summer means, we find again that, within the limits of the probable errors, the range decreases with increasing latitude, Carnsore again showing an abnormally small range. Actually the slight discrepancies between adjacent pairs of stations become still less if seasonal modes are used instead of means, in the diurnal range means were slightly more regular than modes.

The seasonal variation of standard deviation is very consistent. Each one of the six stations has a minimal standard deviation in Spring, all save Peterhead have maximal standard deviation in Summer, (the discrepancy in the Peterhead value is only 1°); the Autumn and Winter values are not very different, and are approximately midway between the Spring and Summer values.

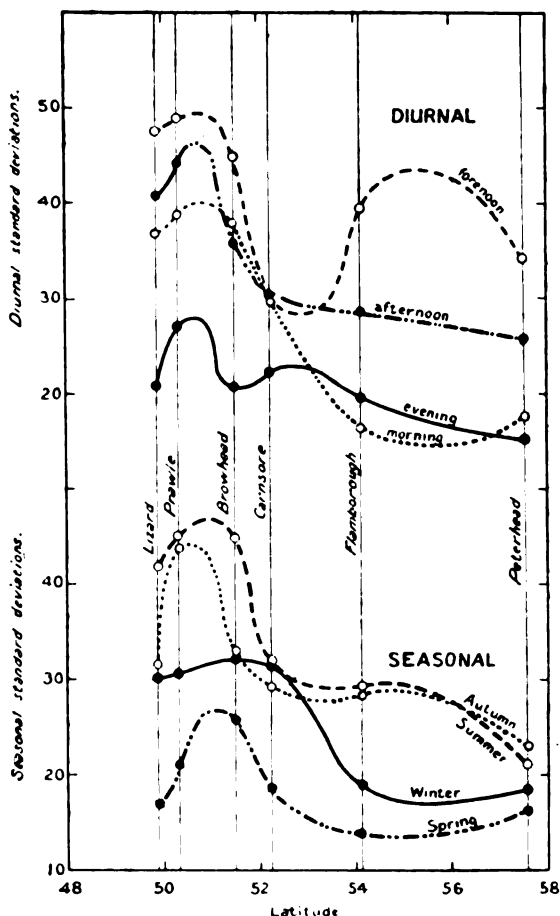
The variation with latitude of the seasonal standard deviations is in strict agreement with the variation of diurnal standard deviations, a general decrease of standard deviation with increasing latitude, Carnsore generally fitting into this scheme but showing slight irregularities, Lizard with consistently lower standard deviations than would follow from the general latitude law. Fig. 4 shows the curves of standard deviation against latitude for the four seasons.

The very uneven distribution in the diurnal groups prevents any clear evidence on diurnal variation of skewness from emerging. The seasonal distribution is, however, much more satisfactory, and the variation in skewness becomes fairly clear. If the difference $X_M - X_F$ be taken as measuring the amount of skew, then Spring shows a positive skew at all stations save the most Northerly one, Summer shows a larger positive skew, decreasing towards the North,

Autumn a positive skew in the South, becoming negative in the North, Winter a negative skew, most negative in the North. Thus Summer and low latitudes tend to give

Fig. 4.

Standard Deviations plotted against Latitude.



positive skews, Winter and high latitudes negative skews, a positive skew being here defined as a clockwise displacement of the mean value from the most frequent value.

VII. *Apparent Locations by Intersection.*

It is not proposed to discuss in this paper the apparent locations of centres of disturbance obtained by plotting on a gnomonic chart the nearly simultaneous observed bearings of atmospherics at several stations. Many such locations have been made, and many have been identified with thunderstorms independently reported by meteorological observers, but an examination of such locations must be reserved for another report.

It is, however, of interest to plot the various modes and means here tabulated. Dealing first with the modal values of all observations for each station, we find that all save Flamborough are contained in a band which, at the point where it cuts the 30° parallel of North Latitude, has a width of 3° , from $6^\circ 20' \text{ E.}$ to $9^\circ 20' \text{ E.}$ The width of the band contributed by the four south-westerly stations just covers the island of Majorca. Browhead, Lizard, and Prawle have modes which intersect at $38^\circ 30' \text{ N.}, 3^\circ 40' \text{ E.}$

The plotting of means instead of modes widens the band, the contribution of the four south-westerly stations now covering both Majorca and Minorca, Browhead, Carnsore and Prawle means intersect $35^\circ \text{ N.}, 6^\circ 20' \text{ E.}$

Of the seasonal values, the Spring modes (excluding Flamborough) form a narrow band crossing the 38° N. parallel between 6° and 8° E. , this being its narrowest section. The South-West group again give a band just within the width of Majorca. The corresponding means cross the 30° N. parallel between 6° and $8^\circ 30' \text{ E.}$, while the Browhead, Lizard, and Prawle means intersect at $38^\circ 5' \text{ N.}, 2^\circ 40' \text{ E.}$

The Summer modes are extremely scattered, the means give a diffuse group of intersections round $46^\circ 30' \text{ N.}, 10^\circ \text{ E.}$

The Autumn modes for Peterhead, Prawle, and Lizard intersect east of Corsica, at $42^\circ 15' \text{ N.}, 9^\circ 40' \text{ E.}$ The means give no intersection and show a slight tendency to converge in the N.W. quadrant.

The Winter modes for the four South-Western stations give a band just wider than Majorca, while Browhead, Lizard, and Prawle give an intersection at $37^\circ \text{ N.}, 4^\circ \text{ E.}$ The means are nearly parallel, the contributions from the South-Western group covering a region from just west of Majorca to just west of Ivica.

In the diurnal groups, the morning and afternoon modes are scattered, the forenoon modes from Prawle, Lizard, and Carnsore give a rather poor intersection at $49^\circ 45' \text{ N.}, 3^\circ 50' \text{ W.},$

the evening modes are nearly parallel. The morning means converge towards N.W., the forenoon means give two alternative intersections, Carnsore, Browhead, and Prawle at 48° N., 3° W., Carnsore, Lizard and Prawle at $49^{\circ} 30'$ N. $3^{\circ} 45'$ W. The afternoon means from Peterhead, Flamborough, Lizard, and Prawle intersect at $45^{\circ} 30'$ N., 14° E., the evening means from the four South-Westerly stations cross the 35° parallel between $7^{\circ} 20'$ and $8^{\circ} 5'$ E.

The "Light" modes from Lizard, Prawle, and Peterhead intersect at 49° N., 8° E., the 0 "Dark" means of Browhead, Carnsore, Lizard, and Prawle cross the 30° N. parallel at 7° and $9^{\circ} 15'$ E.

The "A.M." modes are nearly parallel, the "P.M." modes form a band whose narrowest section is 37° N., $4^{\circ} 20'$ to $5^{\circ} 5'$ E.

The "A.M." means are scattered, the "P.M." means from the four South-Western stations cross the 30° parallel between 10° and 14° E.

In almost all the cases noted above, it will be seen that Flamborough gives bearings pointing eastward of the main bands or intersections. This may be due to "refraction" by the nearly right-angled prism of land formed by Norfolk and Suffolk, some support is lent to this view by the fact that the three cases in which Flamborough falls into the general grouping are cases in which the bearing misses or just grazes this prism, although the cases of crossing to non-crossing are in the ratio of two to one.

The consideration of such refractions would, however, lead too far from the aim of the present paper, as the majority of the rays under consideration cross such land prisms at least once in passing from the Mediterranean to the observing stations.

VIII. *Harmonic Analysis.*

With a view to giving a more precise representation of the Seasonal variations discussed, monthly mean and modal values (without subdivision into diurnal groups) have been computed and the three sets of twelve ordinates, (X_F monthly most frequent direction of maximum disturbance, X_M monthly mean direction, and σ_F monthly standard deviation from X_F) analysed into the series

$$F = (C_0 + C_1 \sin(\phi + X_1) + \dots + C_6 \sin 6(\phi + X_6),$$

where $X_6 = 15^{\circ}$. The coefficients and phase angles are set out in Table II. Their principal features are here enumerated. Owing to the marked disagreement between the

values for Carnsore and those for other stations the rough generalizations that follows are in some cases reached by neglecting Carnsore.

Fourier Coefficients													Table II					
													Approximate date of Maximum occurring nearest to June 15 th					
Station.													1					
C_0 C_1 C_2 C_3 C_4 C_5 C_6													X_1 X_2 X_3 X_4 X_5 X_6					
Monthly mean (mode)	Peterhead	146	15	7	7	9	9	-3	217	98	25	10	66	Feb 5	Apr 26	June 20	June 27	July 9
	Flamborough	138	22	9	8	12	10	-7	215	67	38	3	70	Feb 7	May 4	June 7	July 4	July 5
	Carnsore	152	6	4	1	2	4	-1	72	5	61	25	70	July 3	July 25	Apr 25	June 12	July 5
	Browhead	129	14	10	6	5	15	+8	271	150	110	20	18	Dec 10	Aug 29	July 25	June 17	June 15
	Prawle	130	38	16	9	3	6	-7	222	94	61	32	66	Feb 1	Apr 27	May 15	June 5	July 9
	Lizard	132	28	11	9	14	8	+1	246	126	115	65	70	Jan 6	Mar 26	July 20	July 12	July 5
	Means of Coefficients	138	20	8	7	8	9	-2										
Monthly mean (mean)	Peterhead	146	17	3	4	6	7	0	223	125	8	12	66	Jan 28	Mar 27	July 7	June 25	July 9
	Flamborough	135	25	13	12	16	17	-9	210	82	30	4	64	Feb 12	May 9	June 15	July 3	July 10
	Carnsore	150	4	2	4	2	1	-1	104	157	71	34	64	Jun 2	Aug 22	May 5	June 3	July 11
	Browhead	132	13	11	7	7	13	+4	266	161	107	13	15	Oct 15	Aug 18	July 26	June 24	June 18
	Prawle	133	37	15	8	9	7	-2	275	90	54	21	0	Jan 28	May 1	May 22	June 14	July 4
	Lizard	131	27	12	9	10	10	-3	247	142	100	67	64	Jan 5	Sept 7	Aug 4	July 10	July 10
	Means of Coefficients	135	20	9	8	8	9	-2										
Standard deviation (from monthly mean)	Peterhead	16	5	8	3	5	3	+1	60	50	44	27	7	July 15	June 10	June 1	June 10	June 26
	Flamborough	23	10	7	4	2	4	-1	47	173	85	57	31	July 26	Aug 6	Apr 21	May 11	June 3
	Carnsore	27	5	7	1	1	13	+1	0	39	26	54	16	Sept 14	June 21	June 19	May 14	June 17
	Browhead	34	8	2	4	8	1	-3	62	150	62	14	58	July 13	Aug 29	May 14	June 23	July 17
	Prawle	35	16	4	3	4	4	0	44	52	74	37	55	July 31	June 8	May 2	May 31	July 20
	Lizard	30	9	6	5	1	3	0	42	50	77	38	45	Aug 2	June 10	Apr 20	May 30	May 19
	Means of Coefficients	28	9	6	3	3	5	0										

(a) Most Frequent and Mean Directions of Arrival.

The constant term C_0 varies between 129° for Browhead, and 152° for Carnsore, the mean values do not depart from the modes by more than 3° , and the departures do not appear to be systematic. The considerable difference between the values of C_0 and the corresponding total values in Table I. arise from the very irregular distribution of observations from month to month, and consequent differences of weighting. The unweighted mean value for C_0 for all stations is 138° for both modes and means. This then may be accepted as an approximation to the mean direction of arrival of atmospherics in Great Britain.

The twelve month periodic term has an amplitude C_1 which (excluding the very small value for Carnsore) ranges between 12° and 37° , with a mean for all stations of 20° , again the same whether means or modes are used. The phase angles X_1 lie between 210° and 271° , the corresponding dates of incidence of maximum of this term lying about one month after the winter solstice. The lines of equal amplitude, in so far as they can be plotted with so few stations, have an inclination to the geographical meridians which is approximately midway between that of the isogonics and of the isoclinics of terrestrial magnetism, Peterhead and Browhead, Flamborough and Lizard, forming pairs of

similar amplitude, while Prawle has maximal amplitude. The phase angles X_1 , on the other hand, show a fairly strongly marked longitude variation, increasing Westerly longitude increasing the phase angle, *i. e.* giving an earlier date of maximum clockwise deviation. The actual dates of maximum range from December 10th for Browhead to February 7th for Flamborough in the case of X , for X_M the corresponding dates are December 15th and February 12th.

The same variation is found, with one exception other than Carnsore, in the phase angles X_2 of the six-month term. These indicate in X_F dates of maximum ranging from February 29th for Browhead to June 10th for Flamborough. In the case of X_m the dates of maximum are consistently earlier, by some three weeks on the average. The amplitudes, C_2 , of this term are, in general, less than half the corresponding amplitude C_1 .

The coefficients C_3, C_4 are all of the same order as C_2, C_5 tending to be somewhat larger than C_2 .

To sum up, the analysis reveals a well-marked annual variation, with a range of about 40° , such that the direction of arrival is approximately $138^\circ - 20^\circ = 118^\circ$ E. of N. one month after the summer solstice, and 158° E. of N. after the winter solstice. These deviations are greater in the S.E., less in the N.W., and are reached earlier in the W., later in the E.

The shorter period variations are relatively unimportant. The analysis does not throw much light on the skewness of the distribution. On the mean of all stations the series for X_F and X_M are almost undistinguishable, and the variation of skewness is more obvious in the coarser seasonal groupings previously discussed than in the monthly grouping.

(b) *Standard Deviations from Monthly Most Frequent Values.*

Here the constant term C_0 ranges from 18° at Peterhead to 35° at Prawle, small values of this measure of scattering pertaining to higher latitudes and *vice versa*. Carnsore fits into this general scheme, Lizard, as previously noticed, has smaller scattering than that indicated by latitude effect.

The twelve months' term has an amplitude C_1 lying between 5° for Peterhead and Carnsore and 16° for Prawle. The lines of equal amplitude are similar to the corresponding lines for annual variation of direction of arrival. The phase angles X_1 for this term lie between 0° and 62° , or between 42° and 62° if Carnsore be omitted, the corresponding dates of

maximum standard deviation being August 2nd for Lizard and July 13th for Browhead. Lines of equal phase may also nearly coincide with the lines of equal amplitude: the data are insufficient to decide.

The six months' term has an amplitude C_2 averaging $2/3$ of C_1 , (which is itself about $1/3$ of C_0). This term has a somewhat smaller amplitude in lower latitudes than in higher. The phase angles and higher harmonics have no features of special interest.

The standard deviation from the most frequent direction of arrival has, then, a mean value for the country of 28° , with a variation of twelve months' period giving a maximum standard deviation a month after the summer solstice, this variation having a total range of 18° . The term of six months' period is of some importance, it has a range of 12° and a maximum slightly earlier than that of the annual term. The mean standard deviation in the lower latitudes is about twice that in higher, the annual variation is greater in the S.E. than in the N.W.

IX. Conclusion.

The salient features of the statistical reduction may conveniently be collected here for reference.

The Diurnal Variation of Direction of Arrival has a range of some 35° , a counter-clockwise swing of that amount taking place between the midnight to sunrise period and the noon-sunset period. This diurnal range decreases with increasing latitude, from 58° at Lizard to 22° at Peterhead. The mean is displaced counter-clockwise from the mode at all times save between noon and sunset, and most so between sunset and midnight.

The scattering from the most frequently disturbed direction is generally less in higher latitudes, greatest in sunrise-noon and least in sunset-midnight period.

Observations made during daylight give a mean displaced counter-clockwise by 26° from the mean for dark hour observations. The scattering in daylight is 50 per cent. greater than in the dark.

Observations made before noon are displaced 15° clockwise from those made after noon. The mean of observations after noon is displaced 6° counter-clockwise from the corresponding mode. The scattering before noon is 20 per cent. greater than after noon.

The Seasonal Variation takes a form which, when referred to solar altitude, is similar to the Diurnal. A counter-clockwise swing of some 30° takes place from Spring to Summer.

The mean is displaced clockwise from the mode in Summer and low latitudes, counter-clockwise in Winter and high latitudes. The scattering from the most frequently disturbed direction is least in Spring, greatest in Summer, and is generally less in high latitudes.

The general mean directions of arrival are readily visualized as crossing the island of Majorca.

The mean curves of monthly mean and monthly most frequent directions of disturbance are adequately represented by the expression.

$$X = 138 + 20 \sin (\phi + 230) + 8 \sin 2(\phi + 90),$$

where ϕ is a date measured in days from June 15th.

The scattering from these monthly values is such that some 70 per cent. of all observations will fall within a range of $X_F \pm \sigma_F$ where $\sigma_F = 28^\circ + 9 \sin (\phi + 50) + 6 \sin 2(\phi + 50)$.

The annual variation of direction is large in the S.E., small in the N.W., the maximum deviations from the mean occur earlier in the W., later in the E., and on the mean about a month after the solstices. The semi-annual variation follows a similar law of phase variation with longitude.

The scattering also reaches a maximum about one month after the summer solstice, the mean scattering in lower latitudes is twice that of higher latitudes, and the annual variation of scattering is greater in the S.E. than in the N.W.

It is somewhat unfortunate that the group of stations giving reports sufficiently numerous for full analysis does not include a station in the S.E. of England, to verify these conclusions. Lydd ($50^\circ 58' 20''$ N., $0^\circ 53' 50''$ E.) is well situated, and while its total number of observations reaches only 594, it has been thought worth while to make a partial analysis to test the conclusions that a South-Easterly location favours large annual range, late incidence of annual and semi-annual maxima, large standard deviation, and large annual range of standard deviation.

The results are, considering the paucity of observations, satisfactory. The analysis of monthly mean directions of arrival at Lydd gives a C_0 term of 112° , a C_1 of 70° , an X_1 of 218° , and X_2 of 71° . Thus the annual range is nearly double that of the next station analysed, the annual term has a phase less than 10° (or ten days) out of agreement with the longitude law, the phase of the semi-annual term is in complete agreement with the law. The standard deviations for Lydd give a C_0 term of 38° , C_1 15° , X_1 75° , and X_2 89° . These fit in well with the main results, as they show this

South-Easterly station to have the largest mean standard deviation of all, and an annual range of standard deviation only 1° less than the maximum (that of Prawle).

It would be rash to pursue much further, in face of the obvious limitations of the methods used and of the temporal distribution of the data, the implications of these results. It is sufficient in the present state of our knowledge, to have established in this and the preceding paper *, the essential regularity and simplicity of the general laws emerging from straightforward analysis of data obtained, near the two extremes of the gamut of practical radio frequencies, by standard direction-finding methods. The results themselves must, and must soon, be fitted into a geophysical theory, but their immediate value may rather lie in the encouragement which they offer to the worker seeking order in the superficial disorder of the incidence of naturally occurring electromagnetic waves.

Thanks are due to the Admiralty for the supply of the data and for permission to make use of them in publication, to the Meteorological Office and the Radio Research Board, under whose auspices the work was carried on, to Captain C. J. P. Cave, R.E., and Captain J. A. Slee, R.N., the officers responsible for the inception of the reporting system, and to Mrs. R. A. Watson Watt, who has carried out much the greater part of the reduction of data.

July 3, 1922.

ABSTRACT.

13,000 bearings of atmospherics, taken between 1916 and 1920, at six British coastal direction-finding stations, spread over $7\frac{1}{2}^{\circ}$ in latitude and 9° in longitude, are analysed statistically.

Diurnal and seasonal variations of the apparent direction of arrival of atmospherics are established, the sense of both variations being counter-clockwise with increasing solar altitude. The mean direction of arrival is about 140° E. of N., the mean diurnal range and mean seasonal range are both of the order of 30° , both ranges decrease with increasing latitude. The distribution is skew, the mean being displaced clockwise from the mode (1) in the afternoon, (2) in summer, and (3) in low latitudes, counter-clockwise (1) at other times of the day, (2) in winter, and (3) in high latitudes.

Observations in daylight give a mean displaced 26° counter-clockwise from the mean for dark hour observations. Observations between noon and midnight have a mean 15° counter-clockwise from that for

* *Loc. cit.*

observations between midnight and noon. "P.M." observations show particularly marked skewness, evidently due to the sunset midnight period.

The scattering from the mean or mode for the group, measured by the standard deviation, is great (1) between sunrise and noon, (2) in daylight, (3) A.M., (4) in summer, (5) in low latitudes and small, (1) between sunset and midnight, (2) in darkness, (3) P.M., (4) in spring, (5) in high latitudes.

Fourier analysis of monthly means and modes gives non-periodic terms between 130° and 150° , variations of twelve-monthly period with amplitudes between 4° and 40° , this amplitude being great in the S.E., small in the N.W., the maximum deviation from mean occurring early in the W., late in the E., and on the mean about one month after the solstices. The variation of six-monthly period follows a similar longitude-phase law.

The scattering reaches its maximum about one month after the summer solstice, is less in high latitudes, and its annual range is greater in the S.E. than in the N.W.

These results are tested in the case of a seventh station in S.E. England.

(III. The Calculation of the Skin Effect in Electrical Conductors. By F. F. P. BISACRE, O.B.E., M.A., A.M.Inst.C.E.*

IT is well known that the calculation of the skin effect in straight cylindrical conductors, carrying alternating currents, can be made by means of Bessel Functions of argument $+\sqrt{-j}x$, where $j = +\sqrt{-1}$.

It is usual to split up the required functions into real and imaginary parts, thus:

$$J_0(\sqrt{-j}x) = \text{ber } x + j \text{bei } x = I_0(\sqrt{j}x). \quad (1)$$

$$\frac{d}{dx} J_0(\sqrt{-j}x) = \text{ber}'x + j \text{bei}'x = \frac{d}{dx} I_0(\sqrt{j}x). \quad (2)$$

$$K_0(\sqrt{j}x) = \text{ker } x + j \text{kei } x, \quad (3)$$

$$\frac{d}{dx} K_0(\sqrt{j}x) = \text{ker}'x + j \text{kei}'x. \quad (4)$$

Eight functions therefore enter the general calculation †.

Some years ago the writer had occasion to make calculations of the skin effect in some rather complicated cases.

* Communicated by Sir J. J. Thomson, O.M., F.R.S.

† Russell, Phil. Mag. April 1909, and 'Alternating Currents,' vol. i. p. 207 (1914 Ed.).

He found, as he thought, that there were several objections to the above "ber-bei" method.

1. There are no less than eight functions to handle, to say nothing of the combinations of these; the algebra is consequently very heavy, as Heaviside and Russell have observed.

2. The beauty of the complex variable * seems to be lost if the functions are split up in this way.

3. The symbols for these functions are cumbrous to write, and unless the writing is good, $\text{ber}'x$ degenerates into $\text{bei}x$, $\text{ker}'x$ into $\text{kei}x$, and so on!

Professor Kennelly has published tables for $J_0(\sqrt{-j}x)$ and $J_1(\sqrt{-j}x)$ in his vector notation †, and these are simple to use, but they are applicable only to the solid straight conductor, and the *results* for this case have been tabulated by Pedersen ‡.

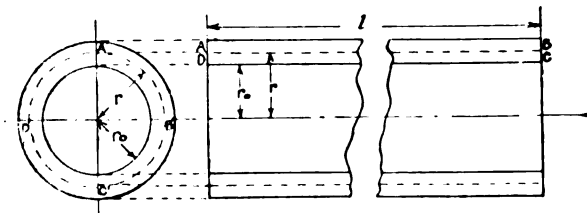
The problem of the single, solid, straight conductor seems, therefore, to have been completely solved. The problems of the straight, tubular conductor and the straight, concentric cable remain.

The author proposes to discuss a method which is readily applicable to these problems and is simple in its numerical use:

Differential Equations.

Let μ be the permeability of the material of the wire, ρ the specific resistance, i the current density at radius r

Fig. 1.



(fig. 1), h the tangential magnetic-field strength at radius r . We assume that the magnetic flux surrounds the wire in circles, the planes of which are perpendicular to the axis of

* As used, for instance, by Sir J. J. Thomson in 'Recent Researches in Electricity and Magnetism' (1893 Ed.; p. 262 *et seq.*).

† Amer. Inst. of Electrical Engineers, vol. xxxiv. no. 8, p. 1795.

‡ *Jahrbuch der Drahtlosen Telegraphie und Telephonie*, vol. iv. pp. 501-515.

the wire and the centres on the axis, and that equipotential surfaces are planes perpendicular to the axis—i. e., the radial current in the wire is ignored.

By applying Faraday's Law of Electromagnetic Induction to the circuit A B C D (fig. 1), we get

$$\rho(i - i_0)l = \frac{\partial}{\partial t} \left[\mu l \int_{r_0}^r h dr \right].$$

$$\therefore \quad \rho \frac{\partial i}{\partial r} = \mu \frac{\partial h}{\partial t} \quad \dots \dots \dots (A)$$

Similarly, by applying the law that the line-integral of the magnetic force round a circuit equals 4π times the current enclosed, we get for A' B' C' D',

$$rh = 4\pi \int_{r_0}^r i r dr.$$

$$\therefore \quad \frac{1}{r} \frac{\partial}{\partial r} (rh) = 4\pi i \quad \dots \dots \dots (B)$$

Equations (A) and (B) are the fundamental differential equations. We can eliminate h or i from these two equations, getting

$$\frac{\partial^2 i}{\partial r^2} + \frac{1}{r} \frac{\partial i}{\partial r} = \frac{4\pi\mu}{\rho} \frac{\partial i}{\partial t} \quad \dots \dots \dots (5)$$

$$\text{and} \quad \frac{\partial^2 h}{\partial r^2} + \frac{1}{r} \frac{\partial h}{\partial r} - \frac{h}{r^2} = \frac{4\pi\mu}{\rho} \frac{\partial h}{\partial t} \quad \dots \dots \dots (6)$$

These equations apply in the material of the wire.

The words "magnetic force" and "current" are used in a generalized sense in the following analysis for any functions that satisfy equations (A) and (B) whether the functions be real or complex. The conditions of a particular problem are then specified just as if these quantities were magnetic forces and currents in a physical sense. The "generalized pressure" follows from equation (19) derived in this way. It is well known—and can be easily proved—that if equations (5) and (6) are solved in complex functions and the solution fitted to the generalized conditions of any special problem, then either the real part or the imaginary part of the solution gives a physical solution corresponding to a real current, magnetic force, and electrical pressure.

*General Solution of the Differential Equation
for Current.*

If i is a sinusoidal function of time, we may assume that i is of the form $Se^{j\omega t}$, where S is a complex function of r only to be determined and $\omega = 2\pi n$, where n is the frequency.

Substituting this value of i in equation (5), we get

$$\frac{d^2S}{dr^2} + \frac{1}{r} \frac{dS}{dr} + k^2 S = 0, \quad \dots \quad (7)$$

where $k^2 = -j \frac{4\pi\mu\omega}{\rho} \dots \dots \dots (8)$

Put $q^2 = \frac{4\pi\mu\omega}{\rho}, \dots \dots \dots (9)$

then $k = \sqrt{-j} q, \dots \dots \dots (10)$

where q is a real number.

The solution of equation (7) is

$$S = c_1 J_0(kr) + c_2 H_0(kr), \quad \dots \dots \dots (11)$$

where $J_0(kr)$ is the Bessel function of the first kind, of zeroth order, and $H_0(kr)$ is a Bessel function of the second kind, of zeroth order.

The complete expression for i runs

$$i = [c_1 J_0(kr) + c_2 H_0(kr)] e^{j\omega t}, \quad \dots \dots \dots (12)$$

where c_1 and c_2 are constants to be found from the conditions of the problem.

Since $\rho \frac{\partial i}{\partial r} = \mu \frac{\partial h}{\partial t}$, we easily get (remembering that $\frac{d}{dx} \cdot J_0(x) = -J_1(x)$),

$$h = \frac{4\pi}{k} [c_1 J_1(kr) + c_2 H_1(kr)] e^{j\omega t}. \quad \dots \dots \dots (13)$$

Equations (12) and (13) involve two constants only, to be determined.

By equation (10), we have

$$k = +\sqrt{-j} q, \text{ the +ve sign by definition,} \\ = q(\cos 45^\circ - j \sin 45^\circ);$$

i. e. $kr = [q, -45^\circ], \dots \dots \dots (14)$

and $kr = [qr, -45^\circ]$, where qr is a real number.

$[qr, -45^\circ]$ is sometimes written $qr \overline{45^\circ}$, a vector of length qr , turned through an angle, -45° , relative to the initial line. This notation seems to have no real advantage over $[qr, -45^\circ]$, and it is more difficult and expensive to print.

The Hankel Functions.

The H functions (*Funktionentafeln*, p. 94)* are used instead of the K or G, as H seems to be the symbol for Bessel functions of the second kind for complex arguments which has not been defined by mathematicians in several different ways †.

There are two Hankel functions, the choice between which depends on whether the imaginary part of the argument is positive or negative. If the imaginary part of z is positive, we use $H_p^{(1)}(z)$, defined by

$$j \frac{\pi}{2} H_p^{(1)}(z) = \alpha J_p(z) - Y_p(z) + j \frac{\pi}{2} J_p(z), \quad . \quad . \quad (15)$$

where $\alpha = (\log 2 - \gamma)$, γ is Euler's constant, and $Y_p(z)$ is the usual Neumann function ‡.

If the imaginary part of z is negative, we use $H_p^{(2)}(z)$, defined by :

$$-j \frac{\pi}{2} H_p^{(2)}(z) = \alpha J_p(z) - Y_p(z) - j \frac{\pi}{2} J_p(z). \quad . \quad (16)$$

The function $H_p^{(1)}(z)$ is used for $z = re^{j\theta}$, $0 < \theta < \pi$, the second, $H_p^{(2)}(z)$, for $z = re^{-j\theta}$, $0 < \theta < \pi$.

In the usual ker-kei notation, we get

$$-j \frac{\pi}{2} H_0^{(2)}(\sqrt{-j} \cdot x) = \ker x + j \operatorname{kei} x. \quad . \quad . \quad (17)$$

The ker-kei notation is employed in the B. A. Tables (1915) and in Russell's 'Alternating Currents,' vol. i. p. 209. The H functions approach zero as the modulus of the argument approaches infinity.

* Jahneke & Emde, '*Funktionentafeln mit Formeln und Kurven*,' Teubner, 1909.

† The theory of these functions is no concern of the applied physicist—it is sufficient for his purpose if he knows their properties and where he can get tables of their values. "The choice of a standard solution" of the second kind "is largely a matter of convention, since the differential equation is still satisfied if we add any constant multiple of $J_n(x)$ " (Lamb, 'Hydrodynamics').

‡ There are some 16 different "standard" solutions, and unfortunately the same letter has often been used in different senses. The relations of the different notations are set out in a table (p. 173, Jahneke & Emde, '*Funktionentafeln*').

‡ Defined p. 93, Jahneke & Emde, '*Funktionentafeln*'.

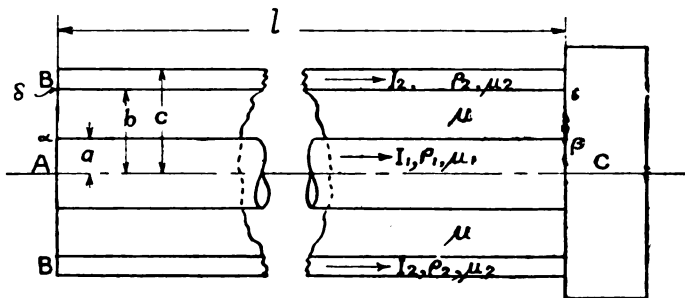
We are only concerned with the $H_p^{(2)}(z)$ function as the imaginary part of the argument is negative; hence we shall write $H_p(z)$ for $H_p^{(2)}(z)$.

The Concentric Cable.

We shall now deal with the problem of the concentric cable.

Suppose (fig. 2) the outer conductor is composed of material of specific resistance ρ_2 and permeability μ_2 , the inner, of specific resistance ρ_1 and permeability μ_1 *, and let μ be the permeability of the material occupying the insulation space.

Fig. 2.



Let I_1 be the total current flowing in the inner at any instant, eastwards, and I_2 the total current in the outer at the same instant eastwards, then $I_1 + I_2 = 0$.

The conditions of potential are that the potential *all over* the end A is constant; all over the end B, constant; and over the short-circuited end C, constant; hence the pressure-drop between A and B is that in the filamental circuit $\alpha\beta + \gamma\delta$. The drop is clearly $l[\rho_1 i_a + \text{drop required to overcome the inductive e.m.f. due to the flux in the insulation space} - \rho_2 i_b]$, the last term having the negative sign because i_b is the current from left to right.

$$\therefore V = l[\rho_1 i_a - \rho_2 i_b + \text{inductive e.m.f. due to insulation-flux}] \quad (18)$$

* The distinction is made mathematically between the properties of the material of the two conductors; but physical facts would have to be taken into account if these properties differed greatly, *e.g.* hysteresis losses, heat-conduction.

When $a < r < b$, $h = \frac{2I_1}{r}$, hence the total flux in the insulation-space is given by

$$\phi = \mu l \int_a^b \frac{2I_1}{r} dr = 2I_1 \mu l \log \frac{b}{a}.$$

$$\therefore V = l \left[\rho_1 i_a - \rho_2 i_b + 2I_1 \mu \log \frac{b}{a} \right]. \quad (19)$$

Now $\rho \frac{\partial i}{\partial r} = \mu \frac{\partial h}{\partial t}.$

$$\therefore \frac{\rho_2}{\mu_2} \left(\frac{\partial i}{\partial r} \right)_b = \left(\frac{\partial h}{\partial t} \right)_b = \frac{\partial}{\partial t} \left(\frac{2I_1}{b} \right) = \frac{2}{b} \frac{\partial I_1}{\partial t}.$$

Similarly

$$\frac{\rho_1}{\mu_1} \left(\frac{\partial i}{\partial r} \right)_a = \frac{2}{a} \frac{\partial I_1}{\partial t}.$$

$$\therefore V = 2l I_1 \left[-\frac{\mu_1 i_a}{a \left(\frac{\partial i}{\partial r} \right)_a} - \frac{\mu_2 i_b}{b \left(\frac{\partial i}{\partial r} \right)_b} + \mu \log \frac{b}{a} \right]. \quad (20)$$

The drop of pressure in the outer is clearly $(-\rho_2 i_b)l$ as there is no flux external to $r=b$; hence, to find the drop in the inner only, we merely have to subtract $(-\rho_2 i_b)l$; hence the pressure-drop along the inner, V_i , is given by

$$V_i = l \left[\rho_1 i_a + \rho_2 (i_c - i_b) + 2I_1 \mu \log \frac{b}{a} \right], \quad (21)$$

and that along outer conductor, V_o , by

$$V_o = -\rho_2 i_b l, \quad (22)$$

giving a total drop, V , of the value stated in equation (19).

This analysis holds, whatever function I_1 may be of time or whatever the distribution of current may be.

To find expressions for the equivalent resistance and reactance for alternating currents, we need a formula for i , the current density, which may be obtained thus:—

The magnetic conditions are :

$$h = \frac{2I_1}{a} \quad \text{at } r=a,$$

$$\frac{2I_1}{b} \quad \text{at } r=b,$$

$$0 \quad \text{at } r=c \text{ and } r>c.$$

By equation (13), if $I_1 = I_1' e^{j\omega t}$, where I_1' may be a complex number, we get, for the inner conductor,

$$\frac{2I_1' e^{j\omega t}}{a} = \frac{4\pi}{k} [c_1 J_1(ka)] e^{j\omega t},$$

since h is finite at $r=0$ and $\lim_{r \rightarrow 0} |H_1(kr)| = \infty$.

$$\therefore c_1 = \frac{k_1}{4\pi} \cdot \frac{2I_1'}{a} \cdot \frac{1}{J_1(ka)}, \quad \dots \dots (22)'$$

where k_1 is the value of k for the material of the inner conductor.

Also
$$\left(\frac{\partial i}{\partial r}\right)_a = \frac{i_a}{k_1} \cdot \frac{J_0(k_1 a)}{J_0'(k_1 a)}, \text{ by equation (12),}$$

where
$$k_1 = \sqrt{-j} \cdot \sqrt{\frac{4\pi\mu_1\omega}{\rho_1}}.$$

Similarly, for the outer conductor

$$\frac{2I_1'}{b} = \frac{4\pi}{k_2} [c_1 J_1(k_2 b) + c_2 H_1(k_2 b)], \text{ by equation (13),}$$

and
$$0 = \frac{4\pi}{k_2} [c_1 J_1(k_2 c) + c_2 H_1(k_2 c)],$$

where
$$k_2 = \sqrt{-j} \cdot \sqrt{\frac{4\pi\mu_2\omega}{\rho_2}}.$$

We now define a function of $k_2 r$ in the following way:—

Put $\Delta_n(k_2 r, k_2 c) = \left\{ \begin{array}{l} J_n(k_2 r), H_n(k_2 r) \\ J_1(k_2 c), H_1(k_2 c) \end{array} \right\}, n \text{ being 0 or } \left. \begin{array}{l} \text{an integer.} \end{array} \right\} \quad (23)$

We shall only need this function for $n=0$ and $n=1$.

Then
$$h = \frac{2I_1'}{b} \cdot \frac{\Delta_1(kr, kc)}{\Delta_1(kb, kc)} e^{j\omega t},$$

for this expression is of the form (13) above and gives the correct values of h when $r=b$ and $r=c$ —and, by equations (12) and (13),

$$\begin{aligned} i &= \frac{k_2}{4\pi} \cdot \frac{2I_1'}{b} \cdot \frac{\Delta_0(kr, kc)}{\Delta_1(kb, kc)} e^{j\omega t}, \\ &= \frac{k_2 I_1'}{2\pi b} \cdot \frac{\Delta_0(kr, kc)}{\Delta_1(kb, kc)} e^{j\omega t} \dots \dots (24) \end{aligned}$$

Also $\frac{d\Delta_0}{dr} = k_2 \Delta_0'$, where $\Delta_0'(r)$ is $\frac{d}{dx} \Delta_0(x)$,

hence
$$\left(\frac{\partial}{\partial r}\right)_b = \frac{1}{k_2} \frac{\Delta_0(k_2 b, k_2 c)}{\Delta_0'(k_2 b, k_2 c)}.$$

Substituting now in (20), we get

$$V = 2l\dot{I}_1 \left[\frac{\mu_1}{k_1 a} \frac{J_0(k_1 a)}{J_0'(k_1 a)} - \frac{\mu_2}{k_2 b} \frac{\Delta_0(k_2 b, k_2 c)}{\Delta_0'(k_2 b, k_2 c)} + \mu \log \frac{b}{a} \right]. \quad (25)$$

But $\dot{I}_1 = I_1' j\omega e^{j\omega t}$.

$$\therefore V = I_1' e^{j\omega t} \left[-\frac{2lj\omega\mu_1}{k_1 a} \frac{J_0(k_1 a)}{J_1(k_1 a)} + \frac{2lj\omega\mu_2}{k_2 b} \frac{\Delta_0(k_2 b, k_2 c)}{\Delta_1(k_2 b, k_2 c)} + 2lj\omega\mu \log \frac{b}{a} \right], \quad (26)$$

in which accented Bessel Functions are replaced by functions of the first order, with sign changed.

The quantity in [] can be put in the form $\alpha + j\omega\beta$, where α and β are, by definition, *real* numbers.

What is the physical significance of these numbers? We know that

$$\begin{aligned} V &= (\alpha + j\omega\beta) I_1' e^{j\omega t} \\ &= \alpha I_1 + \beta \frac{\partial I_1}{\partial t}, \end{aligned}$$

on replacing $I_1' e^{j\omega t}$ by I_1 .

V and I_1 are both complex numbers, representing pressure and current. Let

$$V = V_1 + jV_2,$$

$$I_1 = C_1 + jC_2.$$

On substituting and equating real and imaginary parts, we get

$$V_1 = \alpha C_1 + \beta \frac{\partial C_1}{\partial t},$$

$$V_2 = \alpha C_2 + \beta \frac{\partial C_2}{\partial t}.$$

By the principle mentioned on page 1028, either of these equations gives a real solution of the problem, *i. e.*, a physical

current corresponding to a physical pressure; but either of these equations is exactly the same equation as we should have connecting an e.m.f. and a current in an inductive circuit of resistance α and inductance β ,

$$\therefore \quad \alpha + j\omega\beta = R + j\omega L,$$

where R is the equivalent resistance and L the equivalent self-inductance, i. e.

$$R + j\omega L = 2j\omega \left[-\frac{\mu_1}{k_1 a} \frac{J_0(k_1 a)}{J_1(k_1 a)} + \frac{\mu_2}{k_2 b} \frac{\Delta_0(k_2 b, k_2 c)}{\Delta_1(k_2 b, k_2 c)} + \mu \log \frac{b}{a} \right]. \quad (27)$$

This result is the *accurate* solution of the problem of the complete concentric circuit.

The further analysis of this result is facilitated by study of the Δ functions.

Δ Functions.

The Δ function is straightforward to handle analytically, and, what is even more important in applied physics, it is convenient for numerical calculation and leads to systematic formulæ (e. g. equation (27) above).

Numerical Calculation of Δ 's.

For cases in which the argument has intermediate values—values too large for the “small”-value approximations and too small for the asymptotic ones, the Δ 's must be calculated from tables of the Bessel Functions concerned.

Tables for the following functions are given in $[r, \theta]$ and $[a + jb]$ form:

$$J_0(\sqrt{-j}x), J_1(\sqrt{-j}x), H_0(\sqrt{-j}x), H_1(\sqrt{-j}x).$$

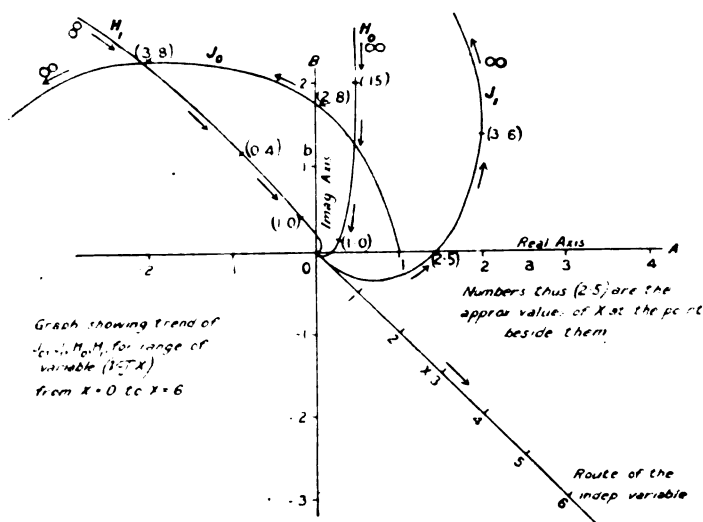
The tables for the J 's in the $[r, \theta]$ form have been calculated from the corresponding tables in the $(a + jb)$ form, due to St. Aldis (Proc. Roy. Soc. Lond. lxvi. pp. 42, 43, 1900). Kennelly also gives a table (Proc. Amer. Inst. Elect. Eng. xxxiv. no. 8, p. 1795) with which this table agrees very closely*. Tables for H_0 and H_1 in the $(a + jb)$ form are due

* The fundamental St. Aldis tables are reprinted in *Funktionentafeln* on pp. 137, 138. In these tables there is an error of sign in the imaginary part from $x=5.1$ to $x=6.0$ inclusive.

to Jahnke and Emde, from *Funktionentafeln*, pp. 139, 140 ; while the $[r, \theta]$ form has been computed from these values*.

The graph (fig. 3) shows the general trend of these functions. The accurate values of Δ_0 and Δ_1 can be computed from these values of the Bessel Functions, for the range $x=0$ to $x=6$. Above $x=6$ asymptotic expressions are available for the direct calculation of the functions required, viz. J_0/J_1 and Δ_0/Δ_1 —and nearly all practical cases are

Fig. 3.



covered by the asymptotic expressions, since the problem of "skin-effect" only becomes of practical importance in "wireless" work where the frequency is high. For this reason, it has not been thought worth while to give approximate formulæ for cases where the variable is small—for such cases, Tables I. and II. are available, while approximate formulæ can be very easily obtained from the series for the Bessel Functions.

* Miss M. M. Fleming and Mr. C. F. Powell have kindly checked these tables independently.

TABLE I.

x.	$J_0(\sqrt{-j}x)=[\rho, \theta]=(a+jb).$				$J_1(\sqrt{-j}x)=[\rho, \theta]=(a+jb).$			
	$\rho.$	$\theta.$	a.	b.	$\rho.$	$\theta.$	a.	b.
0.0	1.0000	0 0 0	+1.0000	+0.0000	0.0000	0 0 0	+0.0000	-0.0000
0.2	1.0001	0 34 23	+1.0000	+0.0100	0.1000	-44 42 59	+0.07106	-0.07036
0.4	1.0003	2 17 29	+0.9996	+0.0400	0.2000	-43 51 56	+0.1442	-0.1386
0.6	1.0020	5 9 11	+0.9980	+0.0900	0.3000	-42 25 12	+0.2215	-0.2024
0.8	1.0064	9 8 32	+0.9936	+0.1599	0.4004	-40 25 16	+0.3048	-0.2596
1.0	1.0158	14 13 13	+0.9844	+0.2496	0.5013	-37 51 11	+0.3958	-0.3076
1.2	1.0319	20 20 26	+0.9676	+0.3587	0.6032	-34 42 6	+0.4959	-0.3434
1.4	1.0586	27 22 13	+0.9401	+0.4867	0.7069	-31 0 35	+0.6059	-0.3642
1.6	1.0984	35 10 13	+0.8979	+0.6327	0.8136	-26 46 0	+0.7264	-0.3664
1.8	1.1544	43 32 49	+0.8367	+0.7953	0.9244	-22 0 2	+0.8571	-0.3463
2.0	1.2291	52 17 31	+0.7517	+0.9723	1.0412	-16 43 45	+0.9971	-0.2997
2.2	1.3247	61 13 2	+0.6377	+1.1610	1.1634	-11 1 33	+1.1419	-0.2225
2.4	1.4429	70 11 24	+0.4890	+1.3575	1.3012	-4 50 10	+1.2966	-0.1097
2.6	1.5856	79 5 23	+0.3001	+1.5569	1.4498	+ 1 42 7	+1.4491	+0.04306
2.8	1.7541	87 52 23	+0.0651	+1.7529	1.6148	8 34 7	+1.5968	+0.2406
3.0	1.9502	96 31 7	-0.2214	+1.9376	1.7998	15 42 54	+1.7326	+0.4875
3.2	2.1761	105 1 57	-0.5644	+2.1016	2.0088	23 4 50	+1.8480	+0.7875
3.4	2.4342	113 25 58	-0.9680	+2.2334	2.2459	30 37 19	+1.9327	+1.1440
3.6	2.7282	121 44 58	-1.4353	+2.3199	2.5155	38 17 45	+1.9742	+1.5589
3.8	3.0613	129 59 28	-1.9674	+2.3454	2.8226	46 3 59	+1.9584	+2.0327
4.0	3.4391	138 11 26	-2.5634	+2.2927	3.1729	53 54 22	+1.8692	+2.5639
4.2	3.8671	146 21 39	-3.2195	+2.1422	3.5722	61 47 24	+1.6886	+3.1479
4.4	4.3518	154 30 47	-3.9283	+1.8726	4.0274	69 42 19	+1.3969	+3.7774
4.6	4.9012	162 39 26	-4.6784	+1.4610	4.5459	77 38 28	+0.9730	+4.4406
4.8	5.5243	170 47 42	-5.4531	+0.8837	5.1366	85 35 27	+0.3949	+5.1214
5.0	6.2313	178 56 0	-6.2301	+0.1160	5.8091	93 33 4	-0.3598	+5.7979
5.2	7.0338	187 4 14	-6.9803	-0.8658	6.5745	101 31 3	-1.3127	+6.4421
5.4	7.9453	195 12 36	-7.6674	-2.0845	7.4456	109 29 31	-2.4844	+7.0189
5.6	8.9821	203 20 52	-8.2466	-3.5597	8.4371	117 28 20	-3.8922	+7.4857
5.8	10.160	211 29 12	-8.6644	-5.3068	9.5510	125 31 18	-5.5492	+7.7735
6.0	11.501	219 37 30	-8.8583	-7.3347	10.850	133 27 8	-7.4622	+7.8767

Columns a & b are by H. Steadman Aldis (Proc. Roy. Soc. Lond. lxi. pp. 42, 43, 1900). Columns ρ & θ computed from a 's and b 's. The signs of the imaginary part in Jahnke & Emde's Table, p. 137, from 5.1 to 6.0. are as in their graph; not as in their Table.

Columns a & b are by H. Steadman Aldis (*loc. cit.*). His figures have been divided by $\sqrt{2}$. Columns ρ & θ computed from a 's & b 's.

TABLE II.

$H_0^{(2)}(\sqrt{-j}x)=[\rho, \theta]=(a+jb).$					$H_1^{(2)}(\sqrt{-j}x)=[\rho, \theta]=(a+jb).$									
	$\rho.$	$\theta.$	$a.$	$b.$		$\rho.$	$\theta.$	$a.$	$b.$					
0.0	∞	90°	0	0	+0.5000	∞	135°	0	0	$-\infty$	$+\infty$			
0.2	1.2042	66	22	29	+0.4826	+1.1033	3.1373	132	24	26	-2.1158	+2.3165		
0.4	0.8114	56	29	10	+0.4480	+0.6765	1.5103	127	30	12	-0.9195	+1.1981		
0.6	0.5995	47	23	59	+0.4058	+0.4413	0.9534	121	33	23	-0.4989	+0.8124		
0.8	0.4617	38	38	33	+0.3606	+0.2883	0.6688	115	0	59	-0.2828	+0.6061		
1.0	0.3641	30	4	43	+0.3151	+0.1825	0.4958	108	6	6	-0.1541	+0.4713		
1.2	0.2918	21	36	56	+0.2713	+0.1075	0.3801	100	56	2	-0.07210	+0.3732		
1.4	0.2366	13	14	36	+0.2303	+0.05420	0.2980	93	35	12	-0.01864	+0.2974		
1.6	0.1933	4	55	23	+0.1926	+0.01659	0.2373	86	6	27	+0.01611	+0.2368		
1.8	0.1591	-	3	21	54	+0.1588	-0.009338	0.1913	78	31	43	+0.03804	+0.1874	
2.0	0.1316	-	11	37	18	+0.1289	-0.02651	0.1555	70	52	17	+0.05096	+0.1469	
2.2	0.1091	-	19	53	23	+0.1026	-0.03712	0.1274	63	9	14	+0.05752	+0.1136	
2.4	0.09112	-	28	5	11	+0.08039	-0.04290	0.1049	55	23	12	+0.05960	+0.08635	
2.6	0.07587	-	36	1	49	+0.06136	-0.04463	0.08684	47	34	51	+0.05858	+0.06411	
2.8	0.06383	-	44	29	55	+0.04553	-0.04474	0.07216	39	44	11	+0.05549	+0.04613	
3.0	0.05367	-	52	39	14	+0.03256	-0.04267	0.06017	31	51	59	+0.05110	+0.03177	
3.2	0.04517	-	60	49	28	+0.02202	-0.03944	0.05032	23	59	8	+0.04598	+0.02046	
3.4	0.03810	-	68	59	30	+0.01366	-0.03557	0.04218	16	4	2	+0.04053	+0.01167	
3.6	0.03219	-	77	9	53	+0.007152	-0.03139	0.03537	8	9	5	+0.03509	+0.005015	
3.8	0.02514	-	85	16	23	+0.002154	-0.02605	0.02990	0	11	3	+0.02984	+0.0009609	
4.0	0.02308	-	93	28	20	-0.001398	-0.02304	0.02517	-	7	46	36	+0.02493	-0.003405
4.2	0.01957	-	101	37	22	-0.003943	-0.01917	0.02126	-	15	44	57	+0.02046	-0.005770
4.4	0.01662	-	109	45	54	-0.005620	-0.01564	0.01798	-	23	43	53	+0.01646	-0.007236
4.6	0.01412	-	117	54	2	-0.006908	-0.01248	0.01523	-	31	43	23	+0.01295	-0.008007
4.8	0.01201	-	126	2	37	-0.007066	-0.009710	0.01291	-	39	42	37	+0.009932	-0.008248
5.0	0.01021	-	134	15	27	-0.007122	-0.007309	0.01096	-	47	43	47	+0.007371	-0.008109
5.2	0.008712	-	142	19	10	-0.006893	-0.005325	0.009310	-	55	44	31	+0.005241	-0.007695
5.4	0.007422	-	150	26	37	-0.006456	-0.003661	0.007917	-	63	45	42	+0.003500	-0.007101
5.6	0.006329	-	158	34	30	-0.005892	-0.002312	0.006737	-	71	47	9	+0.002106	-0.006400
5.8	0.005402	-	166	41	49	-0.005257	-0.001243	0.005738	-	79	48	53	+0.001015	-0.005647
6.0	0.004613	-	174	49	6	-0.004594	-0.0004166	0.004890	-	87	51	4	+0.0001834	-0.004887

Columns a & b from Jahnke & Emde, p. 139, correcting the sign for the real part of $x=6.0$. Columns ρ & θ computed from a 's & b 's.

Columns a & b from Jahnke & Emde, p. 140, correcting the sign of the real part for $x=2.4$. Columns ρ & θ computed from a 's & b 's.

Asymptotic Formulæ.

We require asymptotic formulæ for $\Delta_0(kr, kc)$ and $\Delta_1(kr, kc)$ and, in particular, the ratios

$$\frac{\Delta_0(kb, kc)}{\Delta_1(kb, kc)} \text{ and } \frac{J_0(ka)}{J_1(ka)}.$$

Each of the latter can be obtained directly, without any knowledge of the asymptotic expansions of Bessel Functions, by a physical method *. Take the first one. The function we require an asymptotic expression for is a special value of

$$u_r = \frac{1}{k} \cdot \frac{\Delta_0(kr, kc)}{\Delta_1(kb, kc)}, \text{ viz. } u_b,$$

for then
$$\frac{\Delta_0(kb, kc)}{\Delta_1(kb, kc)} = ku_b.$$

This function, u_r , is clearly a solution of Bessel's Equation

$$\frac{d^2u}{dr^2} + \frac{1}{r} \frac{du}{dr} + k^2u = 0,$$

for it is of the type

$$AJ_0(kr) + BH_0(kr),$$

and
$$\frac{du}{dr} = 0 \text{ when } r = c,$$

$$= -1 \text{ ,, } r = b,$$

and
$$b \leq r \leq c.$$

Put $r = \frac{R}{q}$, and the equation becomes

$$\frac{d^2u}{dR^2} + \frac{1}{R} \frac{du}{dR} + k_1^2u = 0,$$

where
$$k_1 = \frac{k}{q}.$$

The conditions become

$$\frac{du}{dR} = 0 \text{ when } R = qc,$$

and
$$\frac{du}{dR} = -\frac{1}{q} \text{ when } R = qb,$$

and
$$qb \leq R \leq qc.$$

These conditions hold in the region between two concentric tubes of radii qb and qc , the radial gradient of u being

* Dr. J. Dougall suggested this method to the Author.

specified over the inner and outer tubes. Now, when q becomes large, the problem becomes that of finding u for a region between parallel plates, where surfaces of "equal u " are planes parallel to the boundary planes, and the specified radial derivatives become specified normal derivatives over the boundary planes.

Taking the origin in the westward boundary plane and x positive, eastward, we get

$$\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + k_1^2 u = 0^*,$$

where $\frac{\partial^2 u}{\partial y^2} = 0$, to the first order.

$$\therefore \quad \frac{\partial^2 u}{\partial x^2} + k_1^2 u = 0,$$

where $\frac{\partial u}{\partial x} = -\frac{1}{q}$, when $x=0$,

and $\frac{\partial u}{\partial x} = 0$, when $x=q(c-b)$,

whence
$$u = -\frac{1}{k_1 q} \frac{\cos k_1 \{q(c-b) - x\}}{\sin \{k_1 q(c-b)\}},$$

for this value of u clearly satisfies the conditions. Put $x=0$, and we get

$$\begin{aligned} u_b &= -\frac{1}{k_1 q} \cot k_1 q(c-b), \\ &= -\frac{1}{k} \cot k(c-b). \quad \dots \dots (28) \end{aligned}$$

The asymptotic value of $\frac{J_0(ka)}{J_1(ka)}$ can be similarly found, the solid cylinder becoming an infinite plane on the outside and the centre going to infinity, so that the equivalent "rectilinear" figure is a "half-space" bounded by an infinite plane.

$$\text{If} \quad u = \frac{1}{k} \frac{J_0(kr)}{J_1(ka)},$$

we get, asymptotically,

$$\frac{d^2 u}{dx^2} = \lambda^2 u, \text{ where } \lambda = j k_1,$$

* For full details of the transformation of this equation to the Bessel form, see Richardson, 'Electron Theory of Matter,' p. 26 *et seq.*

and
$$\frac{du}{dx} = \frac{1}{q} \text{ when } x=0,$$

$$= 0 \text{ when } x \rightarrow \infty;$$

i. e.,
$$u = -\frac{1}{q\lambda} e^{-\lambda x},$$

which gives, when $x=0$,

$$u_a = -\frac{1}{q\lambda};$$

i. e.
$$\frac{1}{ka} \frac{J_0(ka)}{J_1(ka)} = \frac{j}{ka}, \text{ asymptotically. (29)}$$

The above method is not sufficiently refined to give the accurate asymptotic values of u_r itself for any value of r ; it merely gives the correct values at $r=b$ or $r=a$. The correct values can be found directly from the usual asymptotic formulæ for the Bessel Functions (*Funktionentafeln*, pp. 101, 102). The following values are at once obtained:—

$$\Delta_0(kr, kc) = \frac{2j}{\pi k \sqrt{rc}} \cos k(c-r), \quad (30)$$

$$\Delta_1(kr, kc) = -\frac{2j}{\pi k \sqrt{rc}} \sin k(c-r); \quad (31)$$

i. e.
$$\frac{\Delta_0(kr, kc)}{\Delta_1(kb, kc)} = -\sqrt{\frac{b}{r}} \frac{\cos k(c-r)}{\sin k(c-b)}, \quad (32)$$

and
$$\frac{\Delta_0(kb, kc)}{\Delta_1(kb, kc)} = -\cot k(c-b) = -\frac{\sin \alpha + j \sinh \alpha}{\cosh \alpha - \cos \alpha},$$

where
$$\alpha = \sqrt{2}q(c-b). \quad (33)$$

At very high frequencies.

$$\left. \begin{aligned} \frac{\Delta_0(kb, kc)}{\Delta_1(kb, kc)} &= -j, \\ \frac{J_0(ka)}{J_1(ka)} &= +j. \end{aligned} \right\} \quad (34)$$

while

Numerical Work.

The asymptotic expressions give simple formulæ for numerical work, bearing in mind that Kennelly has given a very useful table of functions of “semi-imaginaries” (see Table VI. of ‘Tables of Complex Hyperbolic and Circular *Phil. Mag.* Ser. 6. Vol. 45. No. 269. May 1923. 3 X .

Functions': Kennelly)*. He gives values of $\sinh$, $\cosh$, $\tanh$, cosech , sech , and coth , where the argument is $[\rho, +45^\circ]$. The numbers are given in $[r, \theta]$ form. Transforming to hyperbolic functions of $[\rho, +45^\circ]$, we get:

$$\Delta_0(kb, kc) = -j \coth \{q(c-b), +45^\circ\}. \quad (35)$$

$$\Delta_0(kb, kc) = \frac{2j}{\pi k \sqrt{bc}} \cosh \{q(c-b), +45^\circ\}. \quad (36)$$

$$\Delta_1(kb, kc) = -\frac{2}{\pi k \sqrt{bc}} \sinh \{q(c-b), +45^\circ\}. \quad (37)$$

Combined Comparative Impedance.

By equation (27), we have

$$R + j\omega L = 2j\omega \left[-\frac{\mu_1 J_0(ka)}{k_1 a J_1(ka)} + \frac{\mu_2 \Delta_0(k_2 b, k_2 c)}{k_2 b \Delta_1(k_2 b, k_2 c)} + \mu \log \frac{b}{a} \right]. \quad (38)$$

Now the areas of the cross-sections of the inner and outer conductors are usually equal, so that

$$a^2 = c^2 - b^2.$$

$$\therefore \frac{a}{c-b} = \frac{c+b}{a},$$

and b and c are each greater than a , therefore a is at least twice as great as $(c-b)$. Hence a higher order of approximation is required with the Δ_0/Δ_1 function than with J_0/J_1 .

We can therefore put

$$J_0/J_1 = j \text{ and } \Delta_0/\Delta_1 = -\cot k(c-b),$$

and R_n , the normal resistance of the whole circuit,

$$= \frac{\rho l}{\pi} \left[\frac{1}{a^2} + \frac{1}{c^2 - b^2} \right] = \frac{\rho l}{\pi} C. \quad (39)$$

Whence,

$$\frac{R + j\omega L}{R_n} = \frac{2\pi\omega}{\rho} \cdot \frac{1}{C} \cdot \left[\frac{\mu_1}{k_1 a} + \frac{\mu_2}{k_2 b} \coth \{q(c-b), 45^\circ\} + j\mu \log \frac{b}{a} \right], \quad (40)$$

where

$$C = \left[\frac{1}{a^2} + \frac{1}{c^2 - b^2} \right],$$

* The following formulæ are useful for transformations:—

$$\cos kx = \cosh (qx, +45^\circ),$$

$$\sin kx = -j \sinh (qx, +45^\circ),$$

$$\cot kx = j \coth (qx, +45^\circ).$$

The right-hand functions are all tabulated in Kennelly's tables, Table VI.

and the "coth" is given directly in Kennelly's Table. In the absence of this table

$$\cot k_2(c-b) = \frac{\sin \alpha + j \sinh \alpha}{\cosh \alpha - \cos \alpha}, \quad \dots \quad (41)$$

where $\alpha = \sqrt{2}q_2(c-b)$ and $k_2(c-b) = \sqrt{-j} q_2(c-b)$. (42)

Example. A concentric copper cable for which

$$a=0.75, \quad b=1, \quad c=1.25, \quad \rho_1=\rho_2=1700, \quad \mu_1=\mu_2=\mu=1.$$

Frequency 345. This relatively low frequency has been specially chosen to test the accuracy of the asymptotic formulæ for values of the variable well within the range of Tables I. & II.

$$q = \sqrt{\frac{4\pi\mu\omega}{\rho}} = 4.0.$$

$C=3.56$ and

$$\begin{aligned} \frac{R+j\omega L}{R_n} &= \frac{2\pi \times 345 \times 2\pi}{1700} \times \frac{1}{3.56} \times \left[\frac{1}{[3.0, -45^\circ]} \right. \\ &\quad \left. + \frac{[1.0746, -27^\circ 3']}{[4.0, -45^\circ]} + j0.2877 \right] \\ &= 1.107 + j1.360. \quad \dots \quad (43) \end{aligned}$$

$$\therefore \quad \frac{R}{R_n} = 1.107, \quad \frac{X}{R_n} = 1.360, \quad \text{and} \quad \frac{Z}{R_n} = 1.752, \quad \dots \quad (44)$$

Z being the equivalent impedance.

It is interesting to compare numerically the accurate and approximate values of J_0/J_1 and Δ_0/Δ_1 at this relatively low value of q .

$$\begin{aligned} J_0(3.00, -45^\circ) &= [1.0836, 80^\circ 48'] \text{ by Tables I. \& II.,} \\ J_1(3.00, -45^\circ) &= [1.0000, 90^\circ] \text{ by } +j \text{ approximation *.} \end{aligned}$$

$$\begin{aligned} \Delta_0(4.00, -45^\circ; 5.00, -45^\circ) &= -[0.9690, 64^\circ 53'] \\ \Delta_1(4.00, -45^\circ; 5.00, -45^\circ) &\text{ by Tables I. \& II.,} \\ &= -[1.0746, 62^\circ 57'] \\ &\text{by } -\cot k_2(c-b), \\ &= -[1.0000, 90^\circ] \\ &\text{by } -j \text{ approx.} \end{aligned}$$

* A closer approximation to $J_0(ka)/J_1(ka)$ is $j\left(1 - \frac{j}{2ka}\right)$.

The Heating of the Conductor.

Consider a coaxial tube of internal radius r and thickness δr , in the material of either conductor.

Let i_r be the complex current density in this tube.

Then, since the physical current is the real part of the current in the tube, $2\pi r \delta r \times i_r$, the heat generated in time δt in this tube is

$$\frac{\rho l}{2\pi r \delta r} \times (\text{real part of } i_r)^2 \times (2\pi r \delta r)^2 \times \delta t. \quad (45)$$

Hence the mean rate at which heat is generated is

$$\frac{\rho l \cdot 2\pi r \cdot \delta r}{T} \int_0^T (\text{real part of } i_r)^2 dt. \quad (46)$$

Now $\frac{1}{T} \int_0^T (\text{real part of } i_r)^2 dt$ is $\frac{|i_r|^2}{2}$ as it is the mean-square of an alternating current whose maximum value is $|i_r|$. Hence, if W_i is the total rate of heat generation in the inner conductor, we get

$$W_i = \rho_1 l \pi \int_0^a |i_r|^2 r dr, \quad (47)$$

and, for the outer conductor,

$$W_o = \rho_2 l \pi \int_b^c |i_r|^2 r dr. \quad (48)$$

Inner Conductor.

$$i_r = \frac{k_1}{2\pi a} \cdot \frac{J_0(k_1 r)}{J_1(k_1 a)} I_1' e^{i\omega t} \text{ by equation (22)',} \quad (49)$$

$$\text{whence} \quad W_i = \frac{\rho_1 l I^2}{2\pi a^2} \int_0^a \left| \frac{J_0(k_1 r)}{J_1(k_1 a)} \right|^2 r dr, \quad (50)$$

where I is the r.m.s. total current flowing.

$$\text{Now} \quad J_0(\sqrt{+j}x) J_0(\sqrt{-j}x) = |J_0(\sqrt{-j}x)|^2$$

because the factors on the left are conjugate complex numbers.

Also, we have the formula

$$\begin{aligned} (m^2 - n^2) \int_0^a r J_0(mr) J_0(nr) dr \\ = a \left[J_0(ma) \frac{\partial}{\partial a} J_0(na) - J_0(na) \frac{\partial}{\partial a} J_0(ma) \right], \quad (51) \end{aligned}$$

* Pidduck, 'A Treatise on Electricity,' p. 13.

whence $\frac{W_i}{R_{n,i} \times I^2} = \text{real part of } \frac{k_1 a}{2} \cdot \frac{J_0(k_1 a)}{J_1(k_1 a)}, \dots$ (52)

where $R_{n,i}$ is the normal resistance of the inner conductor.
(Tables for $\frac{ka}{2} \cdot \frac{J_0(ka)}{J_1(ka)}$ are given in Jahnke & Emde's *Funktionentafeln*, p. 147.)

Outer Conductor.

$$i_r = \frac{k_2}{2\pi b} \cdot \frac{\Delta_0(k_2 r, k_2 c)}{\Delta_1(k_2 b, k_2 c)} I_1' e^{j\omega t} \text{ by (24),}$$

whence $W_0 = \frac{\rho_2 l I^2 q_2^2}{2\pi b^2} \int_b^c \left| \frac{\Delta_0(k_2 r, k_2 c)}{\Delta_1(k_2 b, k_2 c)} \right|^2 r dr. \dots$ (53)

(Compare with (50) above.)

With the help of theorem (51), which is a general one for all Bessel Functions, we can evaluate this integral if we wish, but it is hardly worth while, as the asymptotic formulæ give a very simple result, and it is only where these apply that the additional heating is appreciable.

We get

$$\frac{\Delta_0(k_2 r, k_2 c)}{\Delta_1(k_2 b, k_2 c)} = -\sqrt{\frac{b}{r}} \cdot \frac{\cos k_2(c-r)}{\sin k_2(c-b)}, \text{ by eq. (32),} \quad (54)$$

whence $\left| \frac{\Delta_0}{\Delta_1} \right|^2 r = b \cdot \frac{\cosh \phi + \cos \phi}{\cosh \alpha - \cos \alpha}, \dots$ (55)

where $\phi = \sqrt{2q_2(c-r)}$ and $\alpha = \sqrt{2q_2(c-b)}$.

Integrating, we get

$$W_0 = \frac{\rho_2 l I^2 q_2^2}{2\sqrt{2\pi b}} \times \Phi,$$

where $\Phi = \frac{\sinh \alpha + \sin \alpha}{\cosh \alpha - \cos \alpha}$ and $\alpha = \sqrt{2q_2(c-b)}$. (56)

Putting $R_{n,0}$ for the normal resistance of the outer conductor, we get

$$\frac{W_0}{R_{n,0} I^2} = \frac{(c^2 - b^2) q_2}{2\sqrt{2b}} \times \Phi. \dots$$
 (57)

Whole Circuit.

If R_n is the normal resistance of the whole circuit, $R_n I^2$ is the normal rate of heat-generation. The actual rate is

$(W_0 + W_i) = RI^2$, where R is the equivalent heating resistance.

$$\therefore \frac{R}{R_n} = \frac{\text{actual rate of heat-generation}}{\text{normal rate of heat-generation}} = \frac{W_0 + W_i}{R_n I^2},$$

whence, putting $C = \left[\frac{1}{a^2} + \frac{1}{c^2 - b^2} \right]$ as before, and assuming $\rho_1 = \rho_2$,

$$\frac{R}{R_n} = \frac{1}{C} \left[\text{real part of } \frac{k_1}{2a} \frac{J_0(k_1 a)}{J_1(k_1 a)} + \frac{q_2}{2\sqrt{2} \cdot b} \Phi \right]. \quad (58)$$

By comparing this expression with equation (40) for the equivalent impedance ratio of the whole circuit, it will be found, after a little reduction, that it is the real part of the equivalent impedance ratio, after putting $\frac{J_0(ka)}{J_1(ka)} = j$ as is done in deriving (40). The real part of the first term in (40) gives the energy loss ratio for the inner conductor; of the second term, for the outer; while the log. term is a pure reactance. It therefore seems natural to conclude that the first term in the total equivalent impedance ratio (40) belongs to the inner conductor, the second to the outer conductor, and the third to the inner, as a reactance. In a sense this is true, but it is not true, as we shall now show, that when so interpreted, the r.m.s. voltage across the outer conductor is $Z_o I$, where I is the r.m.s. current flowing, and Z_o the equivalent outer impedance so calculated.

As the frequency tends to infinity the pressure-drop across the outer conductor, and therefore the apparent equivalent impedance, tends to zero—not to infinity, as the second term in (40) does. It is evident that this is so from the fact that, as the frequency increases, the current in the outer conductor concentrates in the inner parts of it, and that $i_c \rightarrow 0$ as $q \rightarrow \infty$, as we shall presently show. There is no flux at all external to $r = c$; hence there can be no inductive e.m.f. on the outside of the outer conductor; and as the current-density on the outside tends to zero as the frequency increases, so, too, must the resistance drop, and hence the e.m.f. across the outer conductor.

The Outer Conductor and the Pressure across it.

$$i_c = \frac{k_2}{4\pi} \cdot \frac{2I_1'}{b} \cdot \frac{\Delta_0(k_2 c, k_2 c)}{\Delta_1(k_2 b, k_2 c)} e^{j\omega t}, \text{ by eq. (24).} \quad (59)$$

Now, by a theorem on linear differential equations of the second order*, we have

$$\Delta_0(k_2 c, k_2 c) = \frac{B}{k_2 c} \text{ where } B \text{ is constant.}$$

* Forsyth, 'Differential Equations,' 3rd ed. p. 181.

This equation is an accurate one; hence we can use the asymptotic expressions to find the value of B. We thus find

$$\Delta_0(k_2c, k_2c) = \frac{2j}{\pi k_2c} \dots \dots \dots (60)$$

If R_0 and L_0 are the *apparent* equivalent resistance and self-inductance of the outer conductor, we get, see (21),

$$(R_0 + j\omega L_0)I_1' e^{j\omega t} = -\rho i_c I,$$

whence
$$\frac{R_0 + j\omega L_0}{R_{n,0}} = \frac{c^2 - b^2}{\pi bc} \cdot \frac{1}{\Delta_1(k_2b, k_2c)} e^{-j\frac{\pi}{2}} \dots \dots (61)$$

This formula is an accurate one.

Putting *Asymptotic Formula.*

$$\Delta_1(k_2b, k_2c) = -\frac{2}{\pi k\sqrt{bc}} \sinh \{q(c-b), 45^\circ\}, \text{ by eq. (31),}$$

we get

$$\frac{R_0 + j\omega L_0}{R_{n,0}} = \frac{(c^2 - b^2)q}{2\sqrt{bc}} \cdot e^{j\frac{\pi}{4}} \cdot \operatorname{cosech} \{q(c-b), 45^\circ\}, \quad (62)$$

where the cosech is tabulated in Kennelly's Tables.

Apparent Impedance of the Outer Conductor as $q \rightarrow \infty$.

The modulus of

$$\operatorname{cosech} \{q(c-b), 45^\circ\} \rightarrow 2e^{-\frac{q(c-b)}{\sqrt{2}}} \text{ as } q \rightarrow \infty,$$

$$\text{and } q \cdot e^{-\frac{q(c-b)}{\sqrt{2}}} \rightarrow 0 \text{ as } q \rightarrow \infty.$$

$$\therefore \frac{R_0 + j\omega L_0}{R_{n,0}} \rightarrow 0 \text{ as } q \rightarrow \infty,$$

i. e. as the frequency increases, the whole pressure-drop across the outer and inner conductors, in series, tends to concentrate on the inner conductor—a result due to the fact that, while the outer conductor is under the magnetic influence of the inner, the inner is screened from the magnetic action of the outer conductor.

At very high frequencies, the formula for the relative apparent impedance becomes

$$\frac{R_0 + j\omega L_0}{R_{n,0}} = \frac{c^2 - b^2}{\sqrt{bc}} q e^{-\frac{q(c-b)}{\sqrt{2}}} e^{-j\left\{\frac{q(c-b)}{\sqrt{2}} - \frac{\pi}{4}\right\}} \dots (63)$$

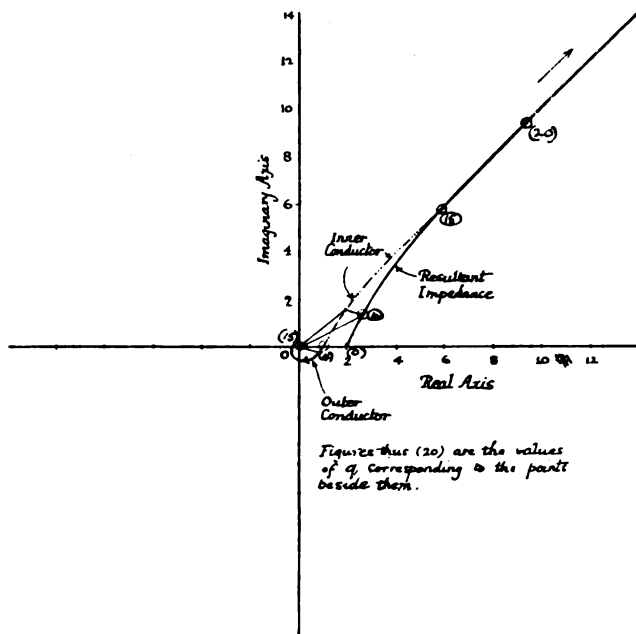
This result shows that, while the apparent impedance approaches zero with increasing frequency, the phase of the

Description of Pressure Vectors.

- OI , current vector.
- Or_1 , in-phase resistance drop in whole circuit.
- r_1R , quadrature reactance drop in whole circuit.
- Or_o , in-phase apparent resistance drop in outer conductor.
- r_oP , quadrature apparent (negative) drop in outer conductor.
- OI_o , total apparent drop in the inner conductor.
- $I_i'I$, quadrature drop in inner conductor due to flux in insulator space.
- OI_i' , true apparent drop in inner conductor.

The general nature of the loci of the ends of the apparent inner and outer impedances and the total (actual) equivalent impedance is shown in fig. 5. The reactance due to the

Fig. 5.



Apparent Impedance Vector Loci, showing effect of increasing frequency (Concentric Cable.)

insulation flux has been omitted, as it increases proportionally with the frequency and rather confuses the point that the diagram is intended to illustrate—namely, the effect of want of uniformity in the current-distribution in the conductors.

CIV. *On Photographing the Ionization Tracks of the Rest Atoms of Radioactive Elements.* By D. M. BOSE, M.A., Ph.D., *Ghose Professor of Physics*, and S. K. GHOSH, M.Sc., *Research Scholar, University College of Science, Calcutta* *.

[Plate XIV.]

WHEN an atom of a radioactive substance disintegrates with the emission of an α -particle, the rest atom recoils back in the opposite direction with a velocity $v' = \frac{m}{m'} v$, where m , v are the mass and velocity of the α -particle, and m' the mass of the rest atom. The value of v' is from 3 to 4×10^7 cm. per sec.

The ionization by these rest atoms has been studied in detail by Wertenstein†. He has shown that though the velocity and kinetic energy of such an atom is about $\frac{1}{5}$ times that of an α -particle, yet the total number of ions produced by such an atom is less than $\frac{1}{100}$ times that produced by an α -particle. On the other hand, he has found that the number of ions produced per cm. length is greater than that produced by an α -particle; in certain cases it was five times greater. Further, contrary to what is observed in the case of α -particles, the number of ions produced per unit length diminishes with the velocity of the rest atom.

The range of the rest atom from RaA was found by Wertenstein to be

In air at atmospheric pressure	0.14 mm.
In hydrogen	0.83 „
In silver about	2×10^{-5} mm.

From the study of the absorption curves he concluded that the scattering of the rest atom is much greater than that of the α -particle, a result which can be expected from theoretical considerations.

It occurred to us that by taking photographs of the ionization tracks of α -particles emitted by the disintegration products of radium emanation contained in a given volume of hydrogen at reduced pressure, it would be possible to get the ionization tracks of the rest atoms too.

* Communicated by the Authors.

† For literature, etc., see Meyer and Schweidler's *Radioaktivität*, pp. 133 & 164. The above account of the ionizing properties of the rest atom has been taken from this book.

From Wertenstein's experiments it was concluded that these tracks would show the following characteristics :—

(i.) They would appear as continuations of the α -particle tracks, but would be thicker at the base and narrower at the end.

(ii.) While the α -particle tracks are straight lines, these would show a considerable amount of scattering.

By means of a modified form of Wilson's apparatus which is described below, we have succeeded in obtaining photographs of the ionization tracks of the rest atoms in hydrogen at a pressure of about 12.5 cm. These tracks show the characteristics which have been mentioned above. It can be stated here at once that, owing to the necessity of having saturated water vapour inside the cloud-chamber the range of the recoiling rest atom inside it, when filled with hydrogen at a given low pressure, is less than what would be expected from Wertenstein's value for the range in hydrogen at atmospheric pressure, viz. 0.85 mm.; *e. g.*, if we take the temperature to be 32° C. (which is about the value that prevailed in the room during this series of experiments), then the tension of saturated water vapour is 3.5 cm., and the range of the rest atom in a vessel filled with hydrogen saturated with water vapour at a pressure of 20 cm. is 1.5 mm. only, while the corresponding value in pure hydrogen under the same pressure is 3.2 mm.

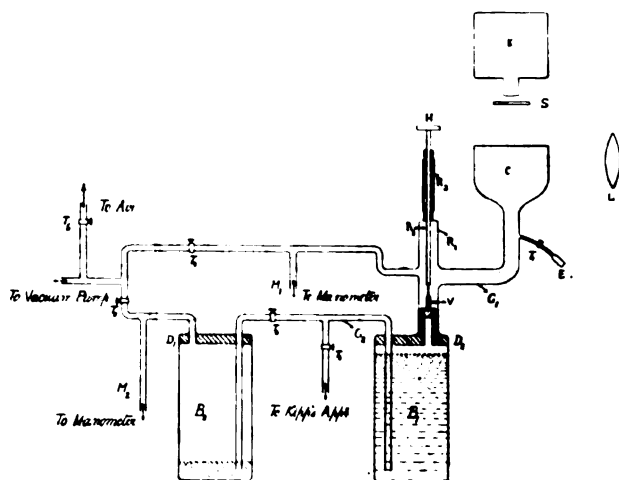
Apparatus.

The essential modification introduced in this apparatus is that while in Wilson's apparatus the expansion is produced by the rapid fall of a piston, here it is produced by opening a valve connecting the cloud-chamber to a vacuum vessel. The apparatus is built on the same principle as the one used by one* of us in photographing the hydrogen recoil atoms. The original apparatus was made entirely of glass, but owing to the difficulty of getting good glass-blowing done here, the present apparatus was made partly of brass. We find that this modification has not in any way diminished the efficiency of the apparatus.

The cloud-chamber C (10 cm. diam. $\times$ 7 cm. depth) is made out of a stoppered-glass bottle, whose bottom is removed and replaced by a glass plate cemented with sealing-wax. To the neck of this bottle is fitted a glass

* D. Bose, *Phys. Zeit.* p. 388 (1916): Berlin Dissertation, 1919.

tube G_1 by means of a ground-glass joint; this tube connects C to the rest of the apparatus. The expansion in C is produced by lifting the valve V and connecting it with the vacuum chamber B_1 . The arrangement for producing a vacuum in B_1 is as follows. Two wide-necked bottles B_1 and B_2 have their openings closed with two wooden disks D_2 and D_1 , which are cemented to the necks with sealing-wax. There are two holes in D_2 , in one of which fits the thick brass tube carrying the valve V and in the other a bent glass tube G_2 which joins B_1 to B_2 . The second glass tube fitted to D_1 connects B_2 either to a Gaede box-pump or to air. The glass bottles are filled partially with water, the level in B_1 being higher than in B_2 . $T_1 \dots T_6$ are glass taps.



A small quantity of radium bromide is contained in the tube E, and the emanation from it can be drawn off to the chamber C by opening T_1 .

To fill the apparatus with hydrogen, all the taps except T_4 are closed and the pump set going. When the air from C and the space above the water-level in B_1 has been sufficiently pumped out, T_4 is closed and hydrogen from a Kipp's apparatus which has passed through two wash-bottles containing water, is introduced into the apparatus by opening T_2 .

After the apparatus has been several times washed out with hydrogen, it is filled with hydrogen at the desired pressure as recorded by the manometer M_1 . To produce an expansion all the taps except T_3 are closed and the pump set going. When the pressure indicated by the manometer M_2 is less than that indicated by M_1 , then T_3 is opened. The level of the water falls in B_1 and rises in B_2 . When the level in B_1 has fallen sufficiently low to produce the required degree of expansion, then T_3 is closed and the pump stopped. On lifting the valve the expansion is produced. The apparatus is brought back to its original state by opening T_6 and T_2 . As the water flows back to B_1 the valve V is lifted up, and the tap T_1 opened. The returning gas sweeps in some of the emanation contained in E into the chamber C .

It is found that when the air in B_1 is being pumped out, some of the hydrogen dissolved in the water bubbles out. After the expansion when air is introduced into B_2 , the water dissolves some of the air, and a part of it is given off to the volume enclosed above the water-level in B_1 . Thus after making a certain number of expansions, it is found necessary to replace the hydrogen in the cloud-chamber, otherwise the ionization tracks of the rest atom cease to be visible.

The cylindrical inner surface of C was completely blackened by covering it with a paste of lampblack mixed with Canada balsam dissolved in xylol. A strip of glass surface was left clear for introducing a beam of sunlight, which was focussed into the chamber by means of a lens L and a heliostat. The camera was placed vertically above the chamber C . A Thornton Pickard shutter S was fitted to the objective of the camera. The releasing string of the shutter was tied to the valve-handle H , after passing over a pair of adjustable pulleys. By adjusting the tension of the string, the exposure can be made at a suitable instant to secure the best photographs of the ionization tracks. Sunlight was only introduced into the chamber after the apparatus had been made ready for an exposure.

The objective used was a Dallmeyer lens of aperture $f/3$. There was an arrangement for removing the ions produced in C by means of an electric field, which was cut off when the exposure was made.

Result.

A few photographs are given (Pl. XIV.) in which are shown the simultaneous ionization tracks of the α -particle and the rest atom arising out of a spontaneously disintegrating radioactive atom. That these photographs represent the beginnings and not the ends of α -particle tracks can be seen from the following considerations.

In these experiments the final pressure in C was about 12.5 cm. (with the exception of No. 1 where it was 15 cm.). Under this pressure in hydrogen the ranges of the α -particles from all the disintegration products of radium are several times the linear dimensions of the vessel. Further, we have found that if no emanation is allowed to enter C by closing the tap T₁, and if the gas in this vessel is removed, then the number of ionization tracks seen at each expansion due to the emission of α -particles from radioactive matter deposited on the inner surface of C is very small; frequently during an expansion not a single track is seen. And these tracks when observed extend from one side of the vessel to the other.

The expansion used in these experiments was about 1.7. The photographs are reproduced on a scale of unit magnification. In all the photographs except No. 4 it will be seen that the ionization tracks are broader at the base and narrower towards the end. All of them show a certain amount of scattering. The rest atom shown in No. 4 we think has been scattered in the direction of the line of sight.

Summary.

A modification of Wilson's expansion apparatus for photographing the tracks of ionizing particles and rays is described.

With this apparatus the ionization tracks of the rest atom of radioactive elements have been photographed.

It was found that these tracks possess the characteristic properties which were deduced by Wertenstein from his study of the ionization produced by rest atoms.

University College of Science,
Physical Laboratory,
Calcutta, India.
Sept. 7, 1921.

CV. *The Elastic Constants of Spruce.* By
H. CARRINGTON, *B.Sc., M.Sc. Tech., A.M.I.Mech.E.**

FROM a consideration of the results of experiments on four balks of spruce †, mean values of the moduli in terms of a unit stress of 10^4 grammes weight per square centimetre are:—

Balk.	E_x .	E_y .	E_z .	F_x .	F_y .	F_z .	μ_{yz} .	μ_{zx} .	μ_{xy} .
A.....	748	421	10,100	24,200	23,000	1,335	621	506	22.65
B.....	864	706	16,900	30,900	45,100	2,170	840	637	35.1
C.....	727	436	10,950	24,500	24,400	1,335	632	506	23.6
D.....	650	424	11,150	23,400	29,100	1,470	602	588	26.1

The axis of z is in the direction of the grain, and the axes of x and y are in directions perpendicular to the grain, and normal and tangential respectively to the annual layers. The direct moduli are noted by E_x , E_y , and E_z ; the symbols F_x , F_y , and F_z are equal respectively to three relations of the type

$$F_x = \frac{E_y}{\sigma_{yz}} = \frac{E_z}{\sigma_{zy}},$$

where $\sigma_{yz} \dots$ denotes $\frac{\text{lateral strain in the direction of } z}{\text{longitudinal strain in the direction of } y}$,

and μ_{yz} , μ_{zx} , and μ_{xy} are the three principal values of the moduli of rigidity.

The moduli correspond with 12 per. cent. of moisture,

* Communicated by the Author.

† Phil. Mag. June 1921, May and July 1922.

and the other physical properties which influence the moduli are:—

Balk.	Density (dry). Grammes/cu.cm.	Shrinkage per cent. in direction.	
		XOX.	YOY.
A	0.371	1.97	3.50
B	0.496	2.86	3.50
C	0.3855	2.15	3.59
D	0.390	1.91	3.84

The elastic constants are the coefficients in the formula for the strain-energy function *

$$2W = Ae_{xx}^2 + Be_{yy}^2 + Ce_{zz}^2 + 2Fe_{yy}e_{zz} + 2Ge_{zz}e_{xx} + 2He_{xx}e_{yy} \\ + Le_{yz}^2 + Me_{zx}^2 + Ne_{xy}^2,$$

this being written in the notation of Love's 'Elasticity.' These coefficients can be calculated from the values of the moduli. Values of A, B, and C are given by three equations of the type

$$A = \frac{1}{\Delta} \frac{E_y E_z}{E_x},$$

and values of F, G, and H by three equations of the type

$$F = \frac{1}{\Delta} \frac{E_x E_z}{E_y},$$

$$\text{where } \Delta = \begin{vmatrix} \frac{1}{E_x} & \frac{1}{E_y} & \frac{1}{E_z} \\ -\frac{1}{F_z} & -\frac{1}{F_y} & -\frac{1}{F_x} \\ -\frac{1}{F_y} & -\frac{1}{F_x} & -\frac{1}{E_z} \end{vmatrix},$$

whilst L, M, and N are equal respectively to μ_{yz} , μ_{zx} , and μ_{xy} .

* Love's 'Elasticity,' Art. 110.

On inserting the values of the moduli given in the first table in these equations, the following table of elastic constants results. The constants are in terms of a unit stress of 10^4 grammes weight per sq. cm.

Balk.	A.	B.	C.	F.	G.	H.	L.	M.	N.
A.....	984	550	11,000	369	564	388	621	506	22.65
B.....	1,100	863	18,150	606	589	437	860	637	38.1
C.....	1,015	607	12,650	424	608	495	632	506	23.6
D.....	1,005	500	11,000	385	579	396	602	588	26.1

It immediately becomes evident from an examination of these results that Cauchy's deduction *, i. e. $F = L$, $G = M$, and $H = N$, does not hold, for H is over ten times as great as N . It therefore follows that the equations of St. Venant †, which were based on the assumption of the truth of this reduction, do not apply. If these equations had held, they would have reduced the number of constants from nine to four. The equations were reduced in default of experimental results for which St. Venant observes the need.

If the spruce can be considered as transversely isotropic, then $A = B$, $F = G$, $L = M$, and $A - 2N = H$, so that the number of constants is reduced from nine to five. It is easily seen that these relations do not apply, and in particular that $A - 2N$ is in every case over twice as great as H . In view of the large number of experiments from which the constants are calculated, the last difference is too great and consistent to be accounted for by variations in the anisotropy of the material.

It accordingly appears that neither Cauchy's reduction nor transverse isotropy hold for spruce. It may be noted that Voigt ‡ found from experiments on the elasticity of crystals that, on the whole, Cauchy's reduction did not apply.

* *Ibid.* Art. 66.

† Todhunter & Pearson's *Elasticity*, vol. ii. Arts 307-314.

‡ Love's *Elasticity*, Art. 113 and Introduction.

CVI. *The Physics of Colour Vision.**By Prof. W. PEDDIE *.*

THE subject of colour vision is one which appeals almost equally to the physicist, the physiologist, and the psychologist. But it is rarely indeed that a writer on the subject is equally qualified to deal with the several aspects. As a matter of fact, it is probable that, with the exception of Helmholtz himself, no one was ever in that position. The experimental physicist deals with the observational facts, and the mathematical physicist deals with their formal relationships. He may, at the same time, introduce a hypothetical mechanism for the elucidation of the reasoning. That mechanism may, or it may not, be ultimately found to be the one actually occurring. The settlement of that question is one for the anatomist or the physiologist. But their settlement of it, when it comes, must be in agreement with the fundamentally essential mathematical formulation as determined by the physicist. And that formulation, developed initially by Helmholtz, is now so complete that the trichromatic theory of vision must be regarded as being established physically, in its main features, on as firm a basis as is the molecular theory, or the electromagnetic theory of light.

Much needless discussion and inconsequent assertions would be prevented were any physiologist, who may happen not to have had the leisure or the training essential to a full comprehension of the bearing of the physical theory, to work out his problems and conclusions in his own way, using his own terminology, and leave its correlation with physical theory to the physicist. There is, for example, no reason really why Dr. Edridge-Green, with his wide observational experience, should not express his results in terms of a score of fundamentals if he so thinks proper. We may leave their subsequent reduction to three, if found possible, to the physicist. The collaboration between the physiologist and the physicist should be complete. Instead of that there is far too often found repeated attacks by physiologists upon certain aspects of physical theory, which are supposed by them to be irreconcilable with facts; the conclusion being due, in many cases, to an insufficient, and probably unavoidably so, familiarity with the physical reasoning.

It is with the hope that this state of matters may become less evident, and that the co-operation of physiologists and

* Communicated by the Author.

physicists may speedily become more complete and fruitful, that I venture to discuss some observational facts, in view of the recent attack by Dr. Edridge-Green upon the trichromatic theory in the November number of this Magazine.

He quotes from Helmholtz the statement that, as far as he could see, there was no means of deciding on the elementary colour sensations other than the examination of the colour-blind. But Dr. Edridge-Green seemingly does not know that this statement has reference necessarily to the early view that colour-blindness was due only to absence of one of the three fundamentals. When Helmholtz found that there were cases of colour-blindness which did not fall into that category, he gave the natural extension of the theory of dichromasy, quite sufficient to cover all observed cases of the abnormality, and more. The result was that he pointed out clearly that it is utterly impossible to discriminate the absolute fundamentals by means of observations on colour mixture. Dr. Edridge-Green surely has not observed that Helmholtz's conclusion is dependent only on the linearity of the law of colour mixture, and is, therefore, quite independent of any assumption as to trichromasy. Thus it applies equally to his own multi-chromatic or non-elemental postulates. Helmholtz's position is exactly counter to Dr. Edridge-Green's aim, instead of supporting it as he claims. His crucial facts are absolutely non-crucial.

In discussing the relation of luminosity to colour he then states, that if the sensation of white were compounded by the addition of three elementary processes, and one of these processes were subtracted, the position of the apex of the luminosity curve would not be the same in the colour-blind as in the normal. Here he must mean that it is to be assumed that the apex of the subtracted curve does not coincide with the luminosity apex. But in any case, it is pointless to refer only to the limited, simplest, and therefore first adopted postulate, as to the mode of occurrence of dichromasy. From this point of view his next statement, that there are numerous dichromics who have a luminosity curve similar to the normal, ceases to have application as an adverse argument. The implied inference is that the trichromatic theory cannot meet the case. On the contrary, this dichromatic type is one of the most easy to predict on the basis of that theory. Then he refers to a case of dichromasy in which there was shortening of the red end of the spectrum while the luminosity apex was in the normal position. This is readily accountable for on the trichromatic theory; but the equation which Dr. Edridge-Green writes down as a trichromatic expression for the

theoretical white is not one which any physicist upholding that theory would write down as the suitable expression.

He then asserts that the facts of colour-blindness are quite inconsistent with any three-sensation theory, and that supporters of such an elemental theory have in many cases contented themselves with describing a case of colour-blindness in the terms of the theory, without showing that the ascertained facts are consistent with the theory. This fairly well amounts to a charge of incompetence, or at the very least, of peculiar oversight. No upholder of the trichromatic theory can claim infallibility: but it is logically impossible to describe in terms of a physical theory, facts which are inconsistent with it. The alternative explanation, which is rendered likely by some of his other statements regarding the theory, is that Dr. Edridge-Green is himself unacquainted with the full scope of the theory. Thus he states, as an example, that no one has shown how, on an elemental theory, 50 per cent. of dangerously colour-blind can get through the now obsolete wool test. If there be any truth in this statement, and it may easily be entirely true, it can only mean that practically everyone is aware of the ease with which the explanation is furnished by the trichromatic theory; in fact, the explanation is identical with that given by Dr. Edridge-Green himself. That it must be so is self-evident to anyone who realizes the essential linearity of the law of colour mixture. Then he asks, as if unanswerable on the trichromatic view, two questions whose solution should be easily given by anyone who realizes the most general way of imposing six relations amongst nine arbitrary quantities.

The next case discussed is one of merely anomalous vision, in which little more than one-half of the normal amount of green was used in forming an equation for white, and fatigue by red diminished the necessary proportion still further. I have known a case of this type in which a colour which was reddish to a normal eye appeared to be greenish to the abnormal eye. The trichromatic explanation is very direct, and Dr. Edridge-Green does not, in this case, make any direct assertion that the effect is not so explainable.

His remarks upon the inadequacy of the terms red-blind and green-blind, as frequently used, may be readily agreed with, although they are only in the same category as other terms, such as latent-heat, which are survivals of an earlier provisional hypothesis, and do no harm when their limitations are comprehended.

He points out the interesting fact that some colour-blind

persons, who object to a normal white equation, cease to do so when the intensity of the comparison white is raised to such an extent that it appears much too bright to the normal eye. He remarks that this clearly shows that the normal mixed white produces the same effect so far as colour is concerned, but has a more powerful effect as to luminosity. This may be so ; but it need not indicate anything more than the change of sensation with intensity. However that may be, when he goes on to say that these facts are quite inconsistent with a hypothetical red sensation, which is affected by light of all visible wave-lengths, it is not possible to agree. He points out that the red end of the spectrum is always shortened in these cases, and, in illustration of his argument, proceeds thus : "A man with shortening of the red end of the spectrum and normal colour discrimination will put together as exactly alike a pink and a blue or violet much darker. If, however, the pink and blue be viewed by a normal-sighted person through a blue-green glass which cuts off the red end of the spectrum, both will appear identical in hue and colour. This proves conclusively that the defect is not due to a diminution of a hypothetical red sensation, because all the rays coming through the blue-green glass are supposed to affect the red sensation, and yet we have been able to correct the erroneous match by the subtraction of red light." Surely it is the case that abstraction of red light from the pink by the blue-green transmitting glass gives rise to less red stimulus, so that the pink looks blue. There is in his statement a fundamental misconception of the implications of the trichromatic theory, which is not by any means uncommon.

The remark is next made that "A totally erroneous view of a case may be obtained through methods based on the three-sensation theory." And, in illustration of this, he discusses a particular case of colour-blindness, and gives an explanation of it, which he apparently presumes to be impossible on the trichromatic theory. Yet the argument could practically be adopted word for word by one accounting for the phenomena on a trichromatic basis.

Finally, Dr. Edridge-Green appeals to Dr. Houstoun's theory as supporting his own special views. It seems to me, on the contrary, that the theory is worthy of consideration as giving a possible indication of the way in which trichromasy has arisen.

He does not seem to be aware of the fact that Helmholtz insisted on the merely illustrative value of the special hypothesis regarding the mechanism of vision, and even said that

a triple set of nerve-fibres might be inessential. The fact that Helmholtz nevertheless did not give up trichomasy might give food for thought. On the other hand, the fact that physiologists very frequently take wrong views of the contents of the trichromatic theory can scarcely be altogether laid to their blame. Knowledge of the earlier developments was spread abroad, and was incorporated in text-books and discussions, and was never superseded fully by the later treatment. Most of the arguments directed against it are futile, in that they are aimed at the older views, and, even so, frequently regard inessentialities as essential. The magnificent structure finally reared by Helmholtz is to this day largely unknown, although it is adequate for the treatment of the most modern work of observation.

CVII. *Quantum Theory of Photographic Exposure.*
*Third Paper. By L. SILBERSTEIN, Ph.D.**

[Communication No. 173, from the Research Laboratory of the
 Eastman Kodak Company.]

THE purpose of this paper is, first, to take account of the absolute energy values of the exposures used in the experiments described in the first two papers on this subject, which values were since measured, and, in the second place, to deduce from the fundamental formula the integral or "density" formula for a certain type of emulsions and to compare it with the experimental results recently obtained with X-rays. The treatment of the first point will afford a good opportunity for amplifying the proposed theory in a sense already hinted at in the second paper.

1. In section 4 of the second paper (Phil. Mag. vol. xliv. 1922, p. 956), it was mentioned that possibly not the whole but only some fraction ϵ of the area a of a silver halide grain is "vulnerable," *i. e.* ready to become developable (say, to lose an electron) on being hit by a light dart carrying a quantum of energy of sufficiently high frequency, and that if n be the unknown number of such darts impinging per unit area of the plate, what can be determined from microphotographic experiments alone is essentially only the product $n\epsilon a$, and therefore also $n\epsilon$, but not n itself. Whether at all and how much the coefficient ϵ , which can be taken as the measure of sensitivity of a given material, differs from unity,

* Communicated by the Author. Paper read at the annual meeting of the American Physical Society at Boston, December 27th, 1922.

can only be decided by measuring the absolute energy-value of the exposure given to the plate. If this be E per cm.² of the plate, we shall have (assuming that the whole energy is split into quantum parcels)

$$E/h\nu = n,$$

and dividing by this number the value of ϵn obtained micro-photographically, we shall find the required value of ϵ .

Now, Trivelli and Righter's "first step" observations which were tabulated in the first paper and for which the microphotographic method gave $\epsilon n = 0.572$ per square micron, *i. e.*

$$\epsilon n = 5.72 \cdot 10^7 \text{ per cm.}^2,$$

was obtained by an exposure to a 250 watt nitrogen lamp at a distance of one metre, through a standardized diaphragm (No. 10) with a standardized opal glass and through a blue filter (referred to as No. 78, giving a maximum intensity at $\lambda = 470\mu\mu$) during 45 seconds. Careful measurements recently completed in this laboratory by Mr. A. L. Schoen have shown that that exposure amounted, within ± 10 per cent., to

$$E = 19.8 \text{ ergs/cm.}^2,$$

i. e., with $\lambda = 470\mu\mu$, to $n = 4.7 \cdot 10^{12}$ light quanta per cm.² of the photographic plate. This also is, substantially, the number of quanta reaching the plane of the (single) layer of grains, for the reflexion at the surface of and the absorption within the thin gelatine layer amount but to a few per cent.

In our case, therefore, *i. e.* for the experimental emulsion W12C used in those observations, the discussed fraction would be as small as

$$\epsilon = 1.2 \cdot 10^{-5}.$$

In fine, on an average, only about one hundred thousandth, and certainly *not more than one ten thousandth*, of the area of a grain of this emulsion would be sensitive to light, *i. e.*, made developable (together with the remainder of the grain) on being hit by a single light dart*. There being good

* Mathematically, the above state of things might be accounted for by assuming that the whole area of a grain is sensitive, but that a "light dart" carries 10^4 or 10^5 quanta of energy. From the physical standpoint, however, such an assumption, made *ad hoc* and standing perfectly isolated, is manifestly very unsatisfactory as compared with that attributing to each light dart a *single energy quantum*. For there is good independent evidence for the existence and separate propagation of precisely such energy parcels.

At first sight yet another alternative might seem possible, namely, to assume that the whole area of a grain is equally "sensitive," but that

reasons for ruling out the alternatives mentioned in the footnote, we are driven to this conclusion by the above experimental results. This does not necessarily mean that only such a small fraction of the impinging light darts is actually absorbed by the grain (the remainder being transmitted and reflected), but that only such a small minority of all these darts are photographically efficient, *i. e.*, do actually eject photoelectrons.

It may be well to point out in this connexion that in a set of Elster and Geitel's experiments (1912) with what was considered a very sensitive potassium cell, only one out of 2300 blue light quanta hitting the cell liberated a photoelectron, though a little later (1913) Pohl and Pringsheim succeeded in pushing the efficiency of a potassium surface under special conditions up to two or even three in a hundred. (Cf. A. L. Hughes, Photo-Electricity, 1914.)

Moreover, the replacing of the measured grain area a by ϵa introduces into the proposed theory, at first purely geometrical, a very desirable feature, namely the coefficient ϵ which may vary from emulsion to emulsion, and will thus serve as a measure of their specific sensitivity. The fact that this coefficient was found to be as small as 10^{-4} or 10^{-5} is also of some practical interest; for it makes it reasonable and worth one's while to try to increase it considerably, pushing it towards its ideal limit, which would be unity.

We have thus far tacitly assumed that, for equal grains at least, ϵ is a given constant fraction, and this amounted simply

instead of one, it must be hit by at least, say, a thousand light quanta in order to be made developable. But such an assumption would entirely distort the original formula

$$k/N = 1 - e^{-s}, \quad s = \text{const. } Ea,$$

which essentially, apart from minor correction terms, does represent the microphotographic findings. In fact, while the number of grains hit at least *once* is

$$k = N(1 - e^{-na}),$$

the number of those hit at least *twice* will be found to be

$$k_2 = k \left(1 - e^{-\frac{m-k}{k}} \right), \quad m = nNa,$$

and the number of those hit *three times*

$$k_3 = k_2 \left[1 - e^{-\frac{m-k_1-k_2}{k_2}} \right],$$

and so on, and these formulæ deviate considerably, and to an increasing extent, from the correct one,

to replacing na in our previous formulæ by nea . The main results will not be altered very much if this simple assumption is replaced by the following more general one which is more likely to correspond to the actual conditions, and seems fruitful inasmuch as it leads to some further interesting experiments.

Let the sensitive part of the area of a grain, instead of being all in a lump, consist of a number of separate vulnerable or *sensitive spots*, each of area ω , and distributed among the individual grains (each of area a) not equally but *haphazardly*. The necessary and sufficient condition for a grain to be made developable will now be that at least one of its spots should be hit by at least one light dart of a sufficiently short wavelength*.

Let N be the total number of grains, of equal areas a , and N_0, N_1, N_2 , etc., the numbers of those among them which have 0, 1, 2, etc., generally κ such vulnerable spots. Then the number of grains affected by an exposure to n light darts will be, by our original formula (without the correction due to a finite "cross-section of the darts," which now may become superfluous),

$$k = \sum_{\kappa=0}^m N_{\kappa} (1 - e^{-\kappa n \omega}),$$

if m be the largest number of spots on a grain. Since

$$N = \sum N_{\kappa},$$

this can be written

$$k = N - \sum_{\kappa=0}^m N_{\kappa} e^{-\kappa n \omega}.$$

Now, if $\bar{\kappa}$ be the average number of spots per grain, the former being distributed haphazardly among the latter, we shall have

$$\frac{N_{\kappa}}{N} = \binom{N\bar{\kappa}}{\kappa} \frac{1}{N^{\bar{\kappa}}} \left(1 - \frac{1}{N}\right)^{N\bar{\kappa} - \kappa},$$

* These vulnerable "spots" will not be confounded with Prof. Svedberg's "centres" (mentioned in our second paper), which he himself considers as the product of light action on the halide grains. The "spots" would rather correspond to the nuclei of sensitiveness suggested by Mr. F. F. Renwick (Brit. Journ. of Photogr. lxviii. 1921, p. 607). It seems likely that Svedberg's "centres" are those of our sensitive spots which were actually hit and thus made developable. If so, then a sufficiently strong exposure should reveal (after a short development) all "spots" as visible markings or "centres."

and for large $N\kappa$ and small $\kappa/N\kappa$,

$$N_k = N \frac{\bar{\kappa}^k e^{-\kappa}}{\kappa!}, \quad (A)$$

and therefore,

$$\frac{k}{N} = 1 - e^{-\kappa} \sum_0^m \frac{\bar{\kappa}^k e^{-\kappa n \omega}}{\kappa!}.$$

Here we can write

$$\Sigma = \Sigma \frac{(\kappa e^{-n\omega})^k}{\kappa!},$$

and if m be a large number (a condition still compatible with a small ratio $m : N\kappa$),

$$\Sigma = e^{\kappa e^{-n\omega}}.$$

Thus our formula becomes

$$k = N[1 - e^{\kappa(e^{-n\omega} - 1)}]. \quad (1)$$

If $n\omega$ (a pure number) is a small fraction, we have

$$e^{-n\omega} - 1 \doteq n\omega,$$

and, as a first approximation,

$$k = N[1 - e^{-n\bar{\kappa}\omega}],$$

as if every grain had actually the average number $\bar{\kappa}$ of spots and, therefore, the same vulnerable area $\kappa\omega$. The second approximation, up to $(n\omega)^2$, will be

$$k = N[1 - e^{-n\kappa\omega(1 - \frac{1}{2}n\omega)}]. \quad (1a)$$

Introducing again the abbreviation

$$v = \log \left(\frac{N}{N-k} \right). \quad (2)$$

the first and the second approximations can more conveniently be written $v = \bar{\kappa}n\omega$ and

$$v = \kappa n\omega(1 - \frac{1}{2}n\omega) \quad (3a)$$

respectively, and the complete formula (1).

$$v = \kappa(1 - e^{-n\omega}). \quad (3)$$

The product $\kappa\omega$ is the average vulnerable area of a grain, and since a is its total (projected) area, our coefficient ϵ , called provisionally "the specific sensitivity," will now be defined by

$$\epsilon = \frac{\bar{\kappa}\omega}{a} = \left(\frac{\bar{\kappa}\omega}{a} \right), \quad (4)$$

and will thus represent the *average sensitivity* of the (equal) grains of the emulsion. We do not prejudice whether ϵ itself is a constant of the material or depends on a . In other words, $\bar{\kappa}$ may but need not be proportional to the area of the grain. Using the definition (4), the approximate formula (3a) can be written

$$v = \epsilon a n (1 - \frac{1}{2} \epsilon a n / \bar{\kappa}). \quad (5a)$$

As far as our present knowledge goes, the second bracketed term need not be a negligible fraction of unity. This will depend on κ . In fact, the value of v observed in all our experiments, even for such grains as $a = 2\mu^2$, was of the order of 0.5. Thus, since $v = \epsilon a n$ gives at least a coarse approximation, the product $\epsilon a n$ itself is, in all these cases, a moderate fraction. Consequently the second term $\epsilon a n / 2\bar{\kappa}$ need not be inappreciably small unless $\bar{\kappa}$, the average number of vulnerable spots per grain, is large.

We will, for the present, close the discussion of the complete equation (3), equivalent to (1), by one more remark. If this equation be accepted as valid even for indefinitely increasing exposure, $\bar{\kappa}$ acquires a simple experimental meaning and is made easily accessible to measurement, namely, it becomes equal to the limiting value of v for $n = \infty$,

$$\bar{\kappa} = v_{\infty} \equiv \log \frac{N}{N - k_{\infty}}, \quad (6)$$

or, equivalently, $k_{\infty} = N(1 - e^{-\bar{\kappa}})$ *. Thus, if $\bar{\kappa}$ is reasonably small, the limiting number k_{∞} of affected grains (of a given size) should perceptibly fall short of the total number N of grains originally present; the surviving grains would simply be those that had no vulnerable spots at all. Whether, and to what extent, such be the case can only be decided by careful experiments with a rather fine-grained emulsion. Notice that if κ amounts to more than a few units, the percentage value of k_{∞} will not be easy to distinguish microphotographically from 100. The utmost which can thus be reliably distinguished can be taken to be 99 per cent., i. e. 1 per cent. surviving grains, to which would correspond $\bar{\kappa} = 4.606$; in order to obtain 10 per cent. of permanently surviving grains, the value of κ would have to be about

* Notice that this is only a verification of (3) with regard to the original assumption, according to which all grains deprived of vulnerable spots (N_0 in number) should be left over. In fact, we have by (A), $N_0 = N e^{-\bar{\kappa}}$, and since, by the said assumption, $k_{\infty} = N - N_0$, formula (6) follows at once.

2.30 only. For small grains, however, $\bar{\kappa}$ may be small enough to enable us to distinguish decidedly k_{∞} from N.

If so, then, having found $\bar{\kappa}$ by means of (6), we shall be able to determine ω by means of (3) which, n being measured, will give

$$\omega = \frac{1}{n} \log \frac{v_{\infty}}{r_{\infty} - r} \quad \dots \quad (7)$$

In this way we may be able to find both κ and ω experimentally, for every grain size a , instead of speculating about their dependence upon a .

The results of experiments just undertaken to that effect by my colleague Mr. Trivelli will be related in the next paper.

2. *Density formula for ideally "exponential" emulsions**.—It has seemed interesting to test the elementary formula $k = N(1 - e^{-n\epsilon a})$ with ϵ assumed constant, by integrating it for an emulsion of exponential type and comparing the resulting formula with the usual density measurements on a plate coated with an emulsion of roughly such a type.

If the number of grains of size a to $a + da$ is $N_a da = f(a) da$, with

$$f(a) = Ce^{-\mu a}, \quad \dots \quad (8)$$

valid from $a = a_1$ to $a = a_2$ (and nil outside these limits), then the total projected area of AgBr made developable will be

$$K = A - \frac{A\mu^2}{(\epsilon n + \mu)^2} \left[1 + (\epsilon n + \mu)a \right] e^{-(\mu + \epsilon n)a} \Bigg|_{a_2}^{a_1},$$

where $A = \int a f(a) da$ is the total available area of the silver halide.

If the frequency curve has a long "tail," as is the case with many emulsions, we can approximate the real case by taking $a_2 = \infty$, and, on the other hand, if a_1 is small enough, we can simplify matters, without much deviating from the actual conditions, by putting $a_1 = 0$. Thus the last formula becomes

$$K = A - \frac{A\mu^2}{(\epsilon n + \mu)^2} \quad \dots \quad (9)$$

The photographic "density" is always assumed to be

* I. e., emulsions whose frequency-curves assume an exponential form, as defined by (8); this is, approximately, the case for many emulsions.

proportional to the blackened mass of silver halide*. If so, then denoting by D_m the "maximum density," or rather the extreme density obtainable,

$$D = D_m \left[1 - \frac{\mu^2}{(\epsilon n + \mu)^2} \right]. \quad (10)$$

Notice that D depends only on the quotient $\epsilon n/\mu$.

On the other hand, if the transparency T of the plate is taken to be

$$T = 1 - K,$$

the corresponding density will be (writing Log for $\log_{10}$)

$$D = -\text{Log } (1 - K), \quad (11)$$

of which the former relation is an approximation (for small K). At any rate, it has seemed interesting to combine also this relation (11) with the formula (9) for the blackened area K . This, with the abbreviation

$$\frac{\epsilon n}{\mu} = \alpha E, \quad (12)$$

gives for the density D as function of the exposure E , in any conventional units,

$$D = -\text{Log} \left[1 - K_m + \frac{K_m}{(1 + \alpha E)^2} \right], \quad (13)$$

where K_m is defined by

$$D_m = -\text{Log } (1 - K_m). \quad (13a)$$

Now, in most practical cases (of many-layered coatings, of course) the extreme density D_m certainly exceeds the value 3, so that $1 - K_m < 0.001$. For plates producing such high densities we may use the limit of (13) for $K_m = 1$ (i. e. for $D_m = \infty$), which gives

$$D = 2 \text{Log } (1 + \alpha E). \quad (14)$$

* This is based on experimental results obtained with *many-layered* coatings for densities ranging from 0.5 to 3.5 (cf. Sheppard and Mees. Investigations on the Theory of the Photographic Process, p. 38). The matter has been investigated mathematically by P. G. Nutting (Phil. Mag. xxvi. p. 423 (1913)). For a one layer coating the proportionality between density and mass of silver does not hold, the correct relation being, manifestly, T (transparency) $= 1 - K$, whence

$$D = \text{Log} \left(\frac{1}{T} \right) = -\text{Log } (1 - K),$$

so that only for small K , $D = MK$, where Log stands for $\log_{10}$, and $M = \text{Log } e$.

It has seemed interesting (even apart from any theory) to compare this remarkably simple formula with some experimental "characteristic curves," especially with X-ray exposure curves which appeared to be qualitatively at least of such a type. Although the relation (11), upon which (14) is based, is suited primarily to single-layer plates, yet the latter formula might be expected to hold also, approximately at least, for many-layered coatings, provided the emulsion has, roughly, an exponential effective frequency curve. The following table contains the results of such a comparison. The first column gives the X-ray exposures E in arbitrary units (in this case, proportional to the exposure times, at reliably constant intensity), and the second column the corresponding densities obtained in this laboratory by Mr. R. B. Wilsey on a "portrait film," the development conditions and time being the same for the whole set of fourteen exposures.

E .	$D_{\text{obs.}}$	$D_{\text{calc.}}$	δD .
1	0.08	0.12	+0.04
$\sqrt{2}$	0.15	0.17	+0.02
2	0.20	0.23	+0.03
$2\sqrt{2}$	0.29	0.30	+0.01
4	0.40	0.41	+0.01
$4\sqrt{2}$	0.54	0.54	0.00
8	0.72	0.69	-0.03
$8\sqrt{2}$	0.90	0.87	-0.03
16	1.10	1.07	-0.03
$16\sqrt{2}$	1.32	1.29	-0.03
32	1.56	1.53	-0.03
$32\sqrt{2}$	1.80	1.79	-0.01
64	2.12	2.06	-0.06
$64\sqrt{2}$	2.48	2.33	-0.15

The third column contains the density values calculated by means of (14). The constant being given the value

$$\alpha = 0.151,$$

all the observations, in the wide range of $E = 1$ to 64, and even to $64\sqrt{2}$, are well represented. The deviations δD are all, with a possible exception of the last, well within the limits of experimental error.

Rochester, N.Y.,
January 23, 1923.

CVIII. *Ionization by Collision in Helium.* By J. S. TOWNSEND, M.A., F.R.S., Wykeham Professor of Physics, Oxford*.

1. **T**HE ionization of argon and helium by the collisions of electrons and positive ions with molecules of the gas was investigated some years ago by Gill and Pidduck †, and the experiments which they made on the currents between parallel plates indicated that these processes of ionization follow the same general laws in the monatomic gases as had previously been found with other gases.

These experiments are not in agreement with the modern views held by some physicists as to the mode of development of currents in monatomic gases, or with the determinations of resonance potentials or ionization potentials as found by experiments where the electrons from a hot filament pass through a gauze between two fields in which the electric forces act in opposite directions.

The apparatus used in the latter experiments resembles the three-electrode valve used in wireless telegraphy; and this method of investigation may be referred to as the valve method in order to distinguish the results from those obtained by measuring the conductivity between parallel plates.

When electrons are emitted from the negative electrode in a gas, and the stream flows to a positive electrode at various potentials, the curve representing the currents in terms of the potentials should, according to the modern theory, be in the form of a series of well-defined steps with angular points at the top and bottom of each step; and when experimental results conflict with this view, the discrepancies are attributed to impurities.

2. I have recently made some experiments with Mr. Ayres on the currents through helium, in order to examine the matter more closely by finding a large number of points on the current-potential curve, as in Gill and Pidduck's earlier experiments these points are far apart, and variations in curvature might have escaped observation. We have taken every precaution to eliminate impurities, and have obtained exactly the same results with helium from a natural source, and helium prepared by heating thorionite. The current-potential curves do not show any steps over the range of forces and pressures similar to those used in Gill and

* Communicated by the Author.

† E. W. B. Gill and F. B. Pidduck, *Phil. Mag.* (6) xvi. p. 280 (1908), and xxiii. p. 837 (1912).

Pidduck's experiments, where the current increased with the potential V , which was proportional to the distance x between the plates, by the factor e^{ax} .

The earlier investigations having been made with a view to testing the theory of ionization by collision and applying it to calculate the sparking potentials, the smallest potentials used in the experiments were generally not less than about 40 or 50 volts. This was necessary in order that the electrons set free from the negative electrode should travel a short distance through the gas and attain the steady motion corresponding to the ratio of the electric force X to the pressure of the gas p .

In the experiments which we have recently made the investigations have been extended, in order to determine the initial effects obtained with comparatively small potentials, where the electrons set free from the negative electrode are being accelerated and begin to acquire sufficient energy to ionize molecules by collisions.

I have recently pointed out in a paper published in the *Philosophical Magazine** some objections to the principles on which the modern theory of the mode of development of currents is founded, assuming the conclusions which have been drawn from the valve experiments to be correct.

In the case of helium the rate of increase of the currents between parallel plates, with the potential difference between the plates, is much greater than the increase which would be obtained if the energy required to ionize a molecule were as great as 21 or 25 volts, which are the minimum ionizing potentials determined by different investigators using the valve method.

It is of importance, therefore, to show how the energy required to ionize a molecule may be investigated by experiments on currents between parallel plates without introducing any hypotheses depending on the lengths of mean free paths of electrons, or on the mode of distribution of energy about the mean value in a group of electrons.

3. When the conductivity between parallel plates is obtained by the action of ultra-violet light on the negative electrode, and the potential difference V between the plates is proportional to their distance apart x , the rate of increase of the current with the potential varies for different ranges of the distance.

In general three ranges may be considered. In the first range, where V is small and the distance x varies from 0 to a , the mean kinetic energy of the electrons and the distribution

* *Phil. Mag.* March 1923.

of the energy about the mean value changes with the distance; in the second range between the distances $x=a$ and $x=b$ the mean kinetic energy of the electrons and the distribution of the energy is independent of the distance x , and the current between the plates is given by the formula $n=n_0e^{ax}$; in the third range from $x=b$ to $x=S$ the positive ions produce an appreciable effect, and sparking takes place at the distance S between the plates. The distances a and b are not very definite and there is no abrupt change in the mode of development of the current. For the purposes of this investigation it is necessary only to consider the rate of increase of the current with the distance between the plates in the first two ranges.

The unit of energy may be taken as the energy acquired by an electron in moving between points differing in potential by a volt, and the energies may be expressed in volts. If c be the energy required to ionize a molecule, ionization may occur when an electron with kinetic energy greater than c collides with the molecule. The probability of a molecule being ionized by a collision depends on the amount by which the energy of the electron exceeds c .

Let $c+\bar{r}$ be the mean energy of the electrons in coming into collisions which result in the ionization of molecules. After a collision the excess of energy $\bar{r}$ may be retained by the colliding electron, or some fraction of it may be imparted to the electron which is set free from the molecule. Hence after the collision the mean energy of these two electrons is $\bar{r}/2$. As these electrons starting with the mean energy $\bar{r}/2$ move through the gas under the action of the electric force, their velocities gradually increase until they again acquire sufficient energy to ionize molecules. The electrons pass through this cycle several times, and in addition to the loss of energy when molecules are ionized, they lose energy in each cycle by collisions with other molecules. Let w be the average value of the total energy lost by each electron in a cycle by collisions with molecules which are not ionized.

4. Let u be the mean energy of the electrons passing any plane between the two planes $x=a$ and $x=b$, where the motion is steady and the distribution of the energies of the electrons about the mean value u is the same at all points between these planes. The number of electrons n that pass through any plane at a distance x from the negative electrode is given by the formula $n=n_0e^{ax}$, which has been found experimentally.

The energy acquired by the stream of electrons as they

Phil. Mag. S. 6. Vol. 45. No. 269. May 1923. 3 Z

pass through the distance $b-a$ is

$$X \int_a^b n_0 e^{ax} dx = \frac{X(n_2 - n_1)}{a},$$

X being the electric force in volts per centimetre, n_1 the number of electrons entering the space through the plane $x=a$, n_2 the number passing out through the plane $x=b$. The energy of the electrons entering the space is $n_1 u$, the energy of those passing out is $n_2 u$, and the energy lost in generating $(n_2 - n_1)$ electrons by collisions is $(n_2 - n_1)c$. Hence

$$\frac{X(n_2 - n_1)}{a} = (c + \bar{u})(n_2 - n_1) + W, \quad . \quad . \quad . \quad (1)$$

where W represents the loss of energy in collisions with molecules which are not ionized. In order to find W in terms of the mean energy w lost in a cycle, the distance $(b-a)$ may be taken as the distance in which the current is doubled, so that $n_2 = 2n_1$. In this case each electron entering the space performs one complete cycle, and the total energy it loses in collisions with molecules which are not ionized is w .

The electrons generated in the space between the planes perform the first part of the cycle, in which their energy increases from the initial mean value $v/2$ to the mean value $\bar{u}$, in moving various distances under the electric force. Thus the new electrons lose less than the original electrons, and their average loss may be represented by $\bar{u}y$, where y is a factor less than .5.

Hence $W = n_1 w(1 + y)$, and equation (1) becomes

$$\frac{X}{a} = c + \bar{u} + \bar{w}(1 + y). \quad . \quad . \quad . \quad . \quad (2)$$

5. A relation between c and r may be obtained by considering the effect of the two groups of electrons passing the plane $x=a$ with the average energies $v/2$ and $c+v$ respectively, when $n_2 = 2n_1$. The factor $e^{(b-a)a}$ is then equal to 2, so that $(b-a) = .693/a$. Thus each electron entering the space between the two planes ionizes one molecule, except some of those with energies less than the mean value $v/2$, the deficiency being made up by some of those with energies greater than the mean value $c + \bar{v}$, which ionize two molecules. The effect as far as the estimate of the mean value of $\bar{v}$ is concerned is the same as if each electron in the two groups ionized one molecule in the space between the two planes. The group passing the plane $x=a$ with the mean energy $\bar{v}/2$

acquires additional energy as it moves under the electric force and ionizes molecules just before passing through the plane $x=b$. The mean loss of energy of each electron in this group due to collisions with molecules which are not ionized is $\bar{w}$, and the energy each acquires under the electric force is $X(b-a)$. Also for each electron entering the space with the energy $\bar{v}/2$ two pass out with the same mean energy, so that the following relation is obtained

$$\frac{X}{\alpha} \times .693 = c + \bar{w} + \bar{v}/2. \quad . \quad . \quad . \quad (3)$$

6. The values of α corresponding to various forces and pressures may be found experimentally, and the ratio α/p may be represented in terms of X/p by means of a curve.

There is a maximum value of the ratio α/X at the point of contact of the tangent through the origin. In helium the value of α/p is .5 and of X/p is 16 at this point, and the corresponding value of $\frac{X}{\alpha} \times .693$ is 22.2 volts. It is therefore

seen from equation (3) that the sum of the three energies ($c + \bar{w} + \bar{v}/2$) has a minimum value which is 22.2 volts, when $X/p = 16$. The energy $\bar{w}$ diminishes and $\bar{v}$ increases as X/p increases, and assuming c to be constant, the variation in the quantity $w + \bar{v}/2$ with the ratio X/p is obtained from the curve representing α/p in terms of X/p .

7. The following expression for u in terms of X/α is obtained by eliminating c from the relation (2) and (3)

$$u = .307 \frac{X}{\alpha} + \frac{\bar{v}}{2} - \bar{w}y, \quad . \quad . \quad . \quad . \quad (4)$$

and it is of interest to find the numbers of electrons with energies above and below the mean value $\bar{u}$ in the space between the two planes $x=a$ and $x=b$.

If $x=a_1$ be a plane near the plane $x=a$, the electrons with the smallest energies which pass the plane $x=a_1$ are those which ionized molecules and the new electrons generated between the two planes. The number ν of these electrons with small energies is $2n_1(\epsilon^{(a_1-a)\alpha} - 1)$, n_1 being the total number passing the plane $x=a$. The electrons which ionize molecules just after passing the plane $x=a$ and those they generate have the largest energies in the group ν , and if the maximum energy is equal to $\bar{u}$ the distance $(a_1 - a)$ is given by the equation

$$\begin{aligned} \bar{u} &= X(a_1 - a) + \bar{v}/2 - \bar{w}y \\ &= .307 X/\alpha + \bar{v}/2 - \bar{w}y. \quad . \quad . \quad . \quad . \quad (5) \end{aligned}$$

3 Z 2

Hence $(a_1 - a) = .307/\alpha$, and the number ν of electrons passing the plane $x = a_1$ with velocities less than u is $2n_1(e^{.307} - 1) = .72n_1$, and the total number passing this plane is $1.36n_1$. Thus 47 per cent. of the total number of electrons passing any plane have energies greater than the mean energy $\bar{u}$.

After passing through the plane $x = a$ the electrons with the larger energies are the first to ionize molecules, and the others acquire sufficient energy to ionize molecules after moving greater distances through the electric field. The electrons which pass the plane $x = a$ with the energy $\bar{u}$ ionize molecules as the stream passes the plane $x = a_2$, where the total number in the stream has increased to $1.47 \times n_1$. Thus $e^{(a_2 - a)\alpha} = 1.47$ and $(a_2 - a) = .385/\alpha$. The potential difference between these two planes is $\frac{X}{\alpha} \times .385$, and in helium the value of this potential is 12.3 volts when $X/p = 16$.

Hence, if the energies of the electrons in a group are all nearly equal to the mean energy $\bar{u}$, when the group is passing a plane $x = a$, the majority of them will ionize molecules near the plane $x = a_2$, which differs in potential from the plane $x = a$ by 12.3 volts when $X/p = 16$. Approximately half the group ionize molecules before and the remainder after passing the plane $x = a_2$.

8. In order to obtain another relation connecting the quantities u , $\bar{u}$, and v , independent of the relations (2) and (3), it is necessary to consider the currents in the gas when the electrons set free from the negative electrode first begin to ionize molecules.

When a group of electrons is set free from the negative electrode by ultra-violet light, the same current is obtained for a considerable range of small distances between the plates when the electric force is maintained constant; but as the distance and potential difference between the plates increases beyond a certain point, the electrons acquire sufficient energy to ionize molecules, and the current increases. They all start with a small velocity from the negative electrode, so that comparatively few of the electrons have energies much different from the mean energy of the group in the earlier stages of their motion through the gas. Thus the mean energy of the group may attain the value $\bar{u}$ before ionization by collision begins to have any appreciable effect on the current. Let N be the number set free from the negative electrode, δ_1 their distance from the electrode when their average energy is $\bar{u}$, δ_2 their distance when half the number in the group N have ionized molecules of the

gas. At this point the number of electrons in the stream is $1.5N$, and the distance δ_2 may be found very accurately from measurements of the currents between the plates at various distances apart when the force X and the pressure p are maintained constant. The preceding investigation shows that if the group of electrons pass the plane $x=\delta_1$ with the mean energy $\bar{u}$, and half the electrons ionize molecules before reaching the plane $x=\delta_2$, the potential difference between the two planes is $\frac{X}{\alpha} \times .385$. Hence

$$X(\delta_2 - \delta_1) = \frac{X}{\alpha} \times .385 \text{ and } \delta_1 = \delta_2 - .385/\alpha.$$

In moving from the negative electrode to the plane $x=\delta_1$ the electrons lose energy by collisions with molecules, and in the latter part of this path, while their energies increase from $\bar{v}/2$ to $\bar{u}$, the average loss of energy is $\bar{w}y$. In the first part of the path, before they attain the energy $c/2$ they lose a comparatively small amount of energy, which may be denoted as $\bar{w}y'$. Hence, if v_0 be the energy of the electrons when emitted from the negative electrode, the following equation for $\bar{u}$ is obtained :

$$\begin{aligned} \bar{u} &= X\delta_1 + v_0 - \bar{w}(y + y') \\ &= X(\delta_2 - .385/\alpha) + v_0 - \bar{w}(y + y'). \quad . \quad . \quad . \quad (6) \end{aligned}$$

The experiments on the initial development of the current from the constant value N to the value $1.5N$ may also be interpreted as showing that when electrons start with energy v_0 and traverse the distance δ_2 under the force X , they attain the average energy $c + \bar{v}$ required to ionize the molecules. This consideration leads to the following relation between the energies :

$$c + \bar{v} = X\delta_2 + v_0 - \bar{w}(1 + y'). \quad . \quad . \quad . \quad (7)$$

The correction for the loss of energy in collisions with molecules which are not ionized is in this case the same as that occurring in the complete cycle while the energy rises from $\bar{v}/2$ to $c + \bar{v}$, and, in addition, the energy $\bar{w}y'$ lost in the collisions which occur before the electrons attain the energy $\bar{v}/2$.

The expression (6) for u may be obtained by eliminating c and $\bar{v}$ from the equations (2), (3), and (7), so that (6) and (7) are not independent relations between the energies.

In determining the values of the quantities $X\delta_2$ and X/α for substitution in the energy equations, the ratio X/p must

be the same in the various experiments. The same values of $X\delta_2$ and X/α are obtained with different pressures and forces, provided the ratio X/p is constant. With the apparatus which has been used, the distance between the plates was not increased above one centimetre, in order to maintain a uniform electric force between the plates; and the most accurate results are obtained by using comparatively small forces and pressures to determine the potential $X\delta_2$, and forces and pressures about three or four times as large to determine α/p . A full account of these experiments will be given in a future paper, but for the purpose of illustrating the method of obtaining the values of $c + \bar{w}$ and $\bar{v}$ it is sufficient to take the value $X\delta_2 = 30.5$ volts obtained when the ratio X/p is 16.

9. The values of $c + \bar{w}$ and $\bar{v}$ obtained from equations (3) and (7) are :

$$c + w = \frac{1.386X}{\alpha} - X\delta_2 - v_0 + \bar{w}y', \quad . \quad . \quad . \quad (8)$$

$$v/2 = X\delta_2 - \frac{.693X}{\alpha} + v_0 - \bar{w}y'. \quad . \quad . \quad . \quad (9)$$

The last two terms in these equations are comparatively small, v_0 being about one volt and $\bar{w}y'$ a quantity of the same order, so that for a first approximation to the values of $c + w$ and $\bar{v}$ these terms may be neglected. When the values of $X\delta_2 = 30.5$ and $X/\alpha = 32$, which were found experimentally, are substituted in the above equations, the following values of the energies are obtained :

$$c + \bar{w} = 14 \text{ volts}, \quad . \quad . \quad . \quad (11)$$

$$\bar{v} = 16.6 \text{ volts}. \quad . \quad . \quad . \quad (12)$$

It is difficult to obtain accurate evidence from these experiments as to the proportion in which the 14 volts is divided between c and $\bar{w}$, but it is improbable that the latter quantity is negligible and c is probably not greater than 12 volts. An investigation is being made of the loss of energy of electrons in collisions with molecules of helium by the same method which has been used with air and other gases, and when it is completed it will be possible to make a more accurate estimate of the value of $\bar{w}$.

The second relation, $\bar{v} = 16.6$ volts, shows that the mean value of the energy of the electrons when they ionize molecules is about 28.6 volts, when the ratio X/p is 16. Hence the energy required to ionize a molecule of helium is approximately 12 volts, and the sum of the energies

of the electron which ionizes the molecule and the electron which is set free is 16.6 volts, after the collision.

In a small proportion of the collisions with energies between 20 and 25 volts, molecules are ionized, but with smaller energies the number which are ionized is inappreciable.

10. There is a considerable difference between the above conclusions and some of those deduced from the valve experiments. It has been found by these experiments that an electron may ionize a molecule of helium by a collision, provided the energy of the electron exceeds a certain minimum value which has been found to be between 21 and 25 volts, and it has been concluded that this number of volts represents the loss of energy of an electron when it ionizes a molecule. This assumption is not, however, supported by experimental evidence, and the direct measurements of the quantity $c+w$ obtained from the results of experiments on the conductivity between parallel plates show that c cannot exceed 14 volts.

The valve experiments have also been interpreted as indicating a comparatively large effect due to radiation from the gas, which may be produced by collisions when the energies of the electrons exceed a certain minimum value called the resonance potential, which is less than the ionizing potential. For helium the resonance potential is about 21 volts, and this number of volts is assumed to represent the loss of energy of an electron when it excites molecular vibrations.

The principal difference between the results of the valve experiments and the parallel-plate experiments is in connexion with the radiation effects. Since the resonance potential is less than the ionizing potential, it is reasonable to assume that collisions which give rise to resonance effects occur more frequently than the collisions in which molecules are ionized, while the energy of the electrons is increased from $\bar{v}/2$ to $c+\bar{v}$ under the action of an electric force. Thus the energy $\bar{w}$ lost in collisions with molecules which are not ionized would be very considerable, and the total loss of energy in a cycle $(c+\bar{w})$ would be very much larger than 14 volts.

CIX. *On the Distribution of Energy in the Lines of the Balmer Series of Hydrogen.* By R. T. BEATTY, M.A., B.E., D.Sc.*

IN the March number of the *Philosophical Magazine* a paper appeared by Prof. P. Lasareff, in which he records visual photometric observations made on a Geissler tube containing hydrogen and excited by a large induction coil. From these observations he obtains the relative energies emitted per second in the lines comprising the first three lines of the Balmer series, and deduces the relative number of atoms which radiate in these three different modes.

This subject was investigated quantitatively some years ago by Jolly † and Beatty ‡. Jolly examined a heavy discharge through hydrogen contained in a silica tube by means of a thermopile. In Beatty's work the hydrogen was excited by a constant current which was kept at a low value to diminish absorption of light by the gas, and energies were measured by a photo-electric cell which was calibrated by a thermopile throughout the spectrum. By using water vapour the continuous background was eliminated.

The following table gives Lasareff's results compared with selected values obtained by Jolly and Beatty:—

	Relative energies.		
	Lasareff (1).	Jolly (2).	Beatty (3).
H _α	1·00	1·00	1·00
H _β	0·34	0·13	0·097
H _γ	0·26	0·053	0·0071
H _δ	...	0·026	0·00093

(1) Heavy disruptive discharge; current and pressure not measured.

(2) Heavy disruptive discharge with condenser: current not measured, pressure 29 mms.

(3) Current 15 milliamperes; pressure 10 mm.

These results differ widely; this is to be expected, as the relative energies are functions of the pressure and current density. Constant values with a simple interpretation may be looked for only when conditions are such that an atom can emit its full radiation without interference by other atoms, and that absorption of the radiation in the tube can be either measured or eliminated.

* Communicated by the Author.

† *Phil. Mag.* (6) xxvi. November 1913, p. 801.

‡ *Phil. Mag.* (6) xxxiii. January 1917, p. 49.

Lasareff, however, disregarding such consideration, has given an interpretation of his results. He argues that since the energy emitted by an atom is $h\nu$, the relative energies in the spectrum lines will give, when divided by the corresponding frequencies ν , the relative number of atoms radiating in each mode.

This argument seems unsound. It neglects the effects of collisions experienced by the radiating atom, the effect of the field of force of neighbouring atoms, the absorption of the radiation by surrounding excited atoms, and the background due to the secondary spectrum of pure hydrogen. It ignores the facts that the relative energies are functions of pressure and current density, that impurities produce a large effect, and that the relative number of atoms and molecules present is influenced by the position of the electrodes and the shape of the Geissler tube.

Much experimental work remains to be done before an answer can be given to the important problem arising out of Niels Bohr's theory of spectra—namely: What is the chance that an atom, which is capable of radiating, shall emit radiation of frequency corresponding to a transition from a given stationary orbit A to another given stationary orbit B?

CX. The Stark Effect for Strong Electric Fields.

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

AFTER a careful study of two papers on the Stark Effect by Mr. A. M. Mosharrafa, which have appeared recently in the *Philosophical Magazine**, I am unable to accept his results without making a small modification. I find that equation (ii.) of the second paper should read

$$N'(n) = (n_1 + n_2 + n_3)^4 \{ 17(n_1 + n_2 + n_3)^2 + 69(n_2 - n_1)^2 - 9n_3^2 \}.$$

Mr. Mosharrafa, in a comparison of the results predicted by his theory with those obtained experimentally by Takamine and Kokubu, finds that the agreement is not as close as could be wished. My results lead to the same value of $N'(n)$ as his, since in all the cases he gives $n_1 = n_2$ and $m_1 = m_2$.

* "On the Appearance of Unsymmetrical Components in the Stark Effect," *Phil. Mag.* May 1922, and "On the Stark Effect for Strong Electric Fields," *Phil. Mag.* August 1922.

But in cases in which the two values of n or m were unequal, the difference would be important.

As pointed out in the second paper, equation (7) * should read

$$B = -\sqrt{A} \left(\sqrt{C} + \frac{nh i}{\pi} \right) + \frac{D}{4A} \left(C - \frac{3B^2}{A} \right) + \frac{5BD^2}{16A^3} \left(3C - \frac{7B^2}{A} \right). \quad (7)$$

Since D^2 contains the factor F^2 , when we substitute for B and B^2 in this equation from (13), we get (to the second order in F)

$$B = -\sqrt{A} \left(\sqrt{C} + \frac{nh i}{\pi} \right) + \frac{D}{4A} \left\{ C - 3 \left(\sqrt{C} + \frac{nh i}{\pi} \right)^2 \pm \frac{F3h^4(n_1 + n_2 + n_3)N \left(\sqrt{C} + \frac{nh i}{\pi} \right)}{32m_0eE^2\sqrt{A}\pi^4} \right\} - \frac{5D^2}{16A^3} \left(\sqrt{C} + \frac{nh i}{\pi} \right) \left\{ 3C - 7 \left(\sqrt{C} + \frac{nh i}{\pi} \right)^2 \right\}. \quad (14)$$

Writing in turn

$$B = m_0(eE + \beta), \quad D = -m_0eF, \quad n = n_1$$

$$\text{and} \quad B = m_0(eE - \beta), \quad D = m_0eF, \quad n = n_2,$$

and in each case $\sqrt{C} = + \frac{n_3 h i}{2\pi}$ (cf. equations (5)), and adding the two resulting equations, we get

$$m_0eE = -\sqrt{A} \frac{(n_1 + n_2 + n_3)h i}{2\pi} + \frac{m_0eF(n_1 + n_2 + n_3)(n_2 - n_1)5h^2}{8A\pi^2} - \frac{3F^2h^5Ni(n_1 + n_2 + n_3)^2}{256A^3\pi^5E^2} - \frac{5m_0^2e^2F^2h^3i}{64A^5\pi^3} \left\{ (n_3 + 2n_1)(n_3^2 + 7n_1n_3 + 7n_1^2) + (n_3 + 2n_2)(n_3^2 + 7n_2n_3 + 7n_2^2) \right\}. \quad (15)$$

This last cubic in $(n_1n_2n_3)$

$$= (n_1 + n_2 + n_3)R,$$

$$\text{where } R \equiv 14n_1^2 + 14n_2^2 + 2n_3^2 + 7n_1n_3 + 7n_2n_3 - 14n_1n_2. \quad (16)$$

* Arabic numerals between 1 and 13 refer to the first of Mr. Mosharafa's papers.

To solve for A, let us put

$$\left. \begin{aligned} A &= -(K + LF + MF^2), \\ \sqrt{A} &= i\sqrt{K} \left(1 + \frac{1}{2} \frac{L}{K} F + \frac{1}{8} \frac{4MK - L^2}{K^2} F^2 \right) \text{ approx.,} \\ \frac{1}{A} &= -\frac{1}{K} \left(1 - \frac{L}{K} F \right) \dots \dots \dots " \\ \frac{1}{A^{3/2}} &= \frac{i}{K^{3/2}} \dots \dots \dots " \\ \frac{1}{A^{5/2}} &= -\frac{i}{K^{5/2}} \dots \dots \dots " ; \end{aligned} \right\} \quad (17)$$

$$\left. \begin{aligned} \therefore m_0 e E &= \frac{h\sqrt{K}}{2\pi} (n_1 + n_2 + n_3) \\ &\quad \times \left(1 + \frac{1}{2} \frac{L}{K} F + \frac{1}{8} \frac{4MK - L^2}{K^2} F^2 \right) \\ &\quad - \frac{3m_0 e h^2 (n_1 + n_2 + n_3)(n_2 - n_1)}{8K\pi^2} \left(1 - \frac{L}{K} F \right) F \\ &\quad + \frac{3h^5 (n_1 + n_2 + n_3)^2 N}{256\pi^5 E^2 K^{3/2}} F^2 \\ &\quad - \frac{5m_0^2 e^2 h^3 (n_1 + n_2 + n_3) R}{64\pi^3 K^{5/2}} F^2 ; \end{aligned} \right\} \quad (18)$$

$$\left. \begin{aligned} \therefore m_0 e E &= \frac{h\sqrt{K}}{2\pi} (n_1 + n_2 + n_3), \\ 0 &= \frac{hL(n_1 + n_2 + n_3)}{4\pi\sqrt{K}} \\ &\quad - \frac{3m_0 e h^2 (n_1 + n_2 + n_3)(n_2 - n_1)}{8K\pi^2}, \\ \text{and } 0 &= \frac{h(n_1 + n_2 + n_3)(4MK - L^2)}{16\pi K^{3/2}} \\ &\quad + \frac{3m_0 e h^2 (n_1 + n_2 + n_3)(n_2 - n_1)L}{8K^2\pi^2} \\ &\quad + \frac{3h^5 (n_1 + n_2 + n_3)^2 N}{256\pi^5 E^2 K^{3/2}} \\ &\quad - \frac{5m_0^2 e^2 h^3 (n_1 + n_2 + n_3) R}{64\pi^3 K^{5/2}}, \end{aligned} \right\} \quad (19)$$

on equating the coefficients of the different powers of F.

. These equations give at once

$$K = \frac{4\pi^2 m_0^2 e^2 E^2}{h^2 (n_1 + n_2 + n_3)^2}, \quad . \quad . \quad . \quad . \quad (20 a)$$

$$L = \frac{3h^2 (n_1 + n_2 + n_3)(n_2 - n_1)}{4\pi^2 E}, \quad . \quad . \quad (20 b)$$

and, after some simplification,

$$M = \frac{h^6 (n_1 + n_2 + n_3)^4}{512\pi^6 m_0^2 e^2 E^4} \left\{ 10R - 54(n_2 - n_1)^2 - \frac{6N}{n_1 + n_2 + n_3} \right\}. \quad . \quad . \quad . \quad (20 c)$$

$$\begin{aligned} \text{Now} \quad N \equiv & (6n_2^2 + 6n_2n_3 + n_3^2)(2n_1 + n_3) \\ & + (6n_1^2 + 6n_1n_3 + n_3^2)(2n_2 + n_3) \end{aligned}$$

(see equation (10), in which there is an obvious misprint of $6n_1n_2$ for $6n_1n_3$),

$$\begin{aligned} \equiv & 3(n_1 + n_2 + n_3)^2 - 3(n_1 + n_2 + n_3)(n_2 - n_1)^2 \\ & - n_3^2(n_1 + n_2 + n_3). \end{aligned}$$

$$\text{Hence} \quad M = \frac{h^6 N'}{512\pi^6 m_0^2 e^2 E^4}, \quad . \quad . \quad . \quad . \quad (21)$$

where

$$\begin{aligned} N' \equiv & (n_1 + n_2 + n_3)^4 \{ 140n_1^2 + 140n_2^2 + 20n_3^2 + 70n_1n_3 + 70n_2n_3 \\ & - 140n_1n_2 - 36(n_2 - n_1)^2 - 18(n_1 + n_2 + n_3)^2 + 6n_3^2 \}, \\ \equiv & (n_1 + n_2 + n_3)^4 \{ 17(n_1 + n_2 + n_3)^2 \\ & + 69(n_2 - n_1)^2 - 9n_3^2 \}. \quad . \quad . \quad (22) \end{aligned}$$

Let W be the energy. Then from equations (5), (20 a), (20 b), and (21),

$$\begin{aligned} W &= \frac{A}{2m_0}, \\ &= \frac{-2\pi^2 m_0 e^2 E^2}{h^2 (n_1 + n_2 + n_3)^2} - \frac{3h^2 (n_1 + n_2 + n_3)(n_2 - n_1)}{8\pi^2 m_0 E} F \\ &\quad - \frac{h^6 N'}{1024\pi^6 m_0^3 e^2 E^4} F^2. \quad . \quad . \quad . \quad (23) \end{aligned}$$

If ΔW denote the change in W due to the introduction of the external field F ,

$$\Delta W = -\frac{3h^2 (n_1 + n_2 + n_3)(n_2 - n_1)}{8\pi^2 m_0 E} F - \frac{h^6 N'}{1024\pi^6 m_0^3 e^2 E^4} F^2. \quad (24)$$

If $\Delta \nu$ be the corresponding change in frequency, Bohr's

formula gives us

$$h\Delta\nu = \Delta W_m - \Delta W_n, \quad . \quad . \quad . \quad (25)$$

where W_m , W_n denote the energies in paths characterized by quantum numbers m_1, m_2, m_3 and n_1, n_2, n_3 respectively.

$$\begin{aligned} \text{Thus, } \Delta\nu = & \frac{3hF}{8\pi^2 m_0 E} [(n_2 - n_1)(n_1 + n_2 + n_3) \\ & - (m_2 - m_1)(m_1 + m_2 + m_3)] \\ & + \frac{h^2 F^2}{1024 \pi^6 m_0^3 e^2 E^4} [N'(n) - N'(m)]. \quad . \quad (26) \end{aligned}$$

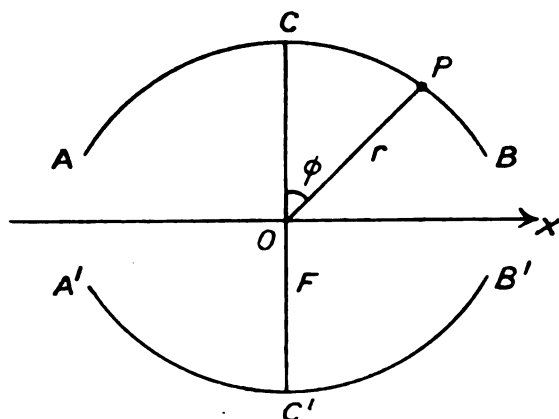
Balliol College, Oxford,
10th February, 1923.

Yours truly,
H. O. NEWBOULT.

CXI. The Spectrum of the Semi-circular Helium Model.

By H. O. NEWBOULT, B.A., Scholar of Balliol College, Oxford.*

SOME time ago Langmuir put forward a model of the helium atom, in which the electrons vibrate about the nucleus in opposite directions†. In the accompanying diagram, the orbits are ACB, A'C'B', and they are reflexions



of each other in an axis Ox , through the nucleus O . By the method of successive approximations and mechanical integration, Langmuir showed that the orbit ACB is very nearly an arc of a circle, whose centre F lies on the perpendicular to Ox through the nucleus.

* Communicated by Dr. J. W. Nicholson, F.R.S.

† See the *Physical Review*, 2nd Series, xvii, p. 339.

The ordinary Sommerfeld-Wilson quantum condition $\int p dq = nh$, when applied to this model, gives a negative value for the ionizing potential, and therefore the model is untenable unless the quantum conditions are modified. Langmuir suggested that the maximum angular momentum of a single electron should be set equal to $\frac{h}{2\pi}$, and deduced

as the value of the ionizing potential 25.62 volts, in close agreement with the experimental value of $25.4 \pm .25$ volts obtained by Franck and Knipping.

Langmuir does not discuss the question of the spectrum of helium; but if his hypothesis is correct, it would appear that the spectrum should be obtained by setting the maximum angular momentum of an electron equal to an integral multiple of $\frac{h}{2\pi}$. In this model it is clear that the maximum angular momentum of the electron which vibrates in the path ACB is attained at the middle point C. If OC is r_0 and the angular velocity at C is $\dot{\phi}_0$, we obtain as our quantum condition,

$$m_0 r_0^2 \dot{\phi}_0 = \frac{nh}{2\pi}, \quad \dots \dots \dots (1)$$

where m_0 is the mass of an electron, and n is an integer.

Now, Langmuir proves that if $-W$ is the total energy of the system,

$$\frac{W r_0}{e^2} = 2N - \frac{1}{2} - \alpha, \quad \dots \dots \dots (2)$$

where Ne is the nuclear charge and

$$\alpha = \frac{m_0 r_0^3 \dot{\phi}_0^2}{e^2}, \quad \dots \dots \dots (3)$$

and obtains as the value of α ,

$$\alpha = 2.0920. \quad \dots \dots \dots (4)$$

From (1) and (2) we get

$$m_0 r_0 e^2 = \frac{n^2 h^2}{4\pi^2 \alpha}, \quad \dots \dots \dots (5)$$

and from (2), on putting $N=2$ for helium,

$$\begin{aligned} W &= \frac{e^2(7-2\alpha)}{2r_0}, \\ &= \frac{2m_0 e^4 \pi^2 \alpha (7-2\alpha)}{h^2} \frac{1}{n^2}. \quad \dots \dots \dots (6) \end{aligned}$$

Hence the frequency of the spectrum should be given by

$$\nu = \frac{\alpha(7-2\alpha)2m_0\pi^2e^4}{h^3} \left(\frac{1}{m^2} - \frac{1}{n^2} \right),$$

$$= \alpha(7-2\alpha)R \left(\frac{1}{m^2} - \frac{1}{n^2} \right), \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where R is the Rydberg constant and m and n are integers.

The formula (7) cannot accord with the ordinary series in the spectrum of helium ; but this fact would not preclude the temporary existence of helium atoms of the structure considered in sufficient numbers to show perhaps a weak spectrum. Thus a test of the formula numerically is desirable in order to determine whether it can lead to any lines associated with helium but not belonging to the ordinary series.

$m.$	$n.$	$\lambda.$	$\nu.$
3	4	3183.83	31408.8
4	5	6878.64	14537.8
4	6	4457.36	22434.8
4	7	3676.94	27196.5
4	8	3301.74	30287.0
5	6	12662.9	7897.06
5	7	7899.68	12658.7
5	8	6349.51	15749.2
5	9	5596.57	17868.1
5	10	5158.98	19383.7
5	11	4821.02	20505.1
5	12	4682.10	21358.0
6	7	21001.0	4761.68
6	12	13460.9	7428.92

The values of m and n in the table were selected with a view to obtaining wave-lengths in the visible spectrum. The first line and the last two show that such lengths can only be given by $m=4$ or 5 .

The spectrum does not show a correspondence with any known spectrum ; and the only conclusion that can be made is that the hypothesis about the quantum condition used in Langmuir's investigation is not correct, though it does lead to a suitable value of the ionizing-potential.

CXII. *Adsorption from the Gas Phase at a Liquid-Gas Interface.*—Part I. By THOMAS IREDALE*.

IT was proposed to measure the adsorption at a liquid-gas interface of a substance which is present, not in solution in the liquid phase but as a constituent of the gas phase only. The idea is not new (Gibbs, *Scientific Papers*, vol. i. p. 235; Cantor, *Annalen der Physik*, vol. lvi. p. 492, 1895; Langmuir, *Journ. Amer. Chem. Soc.* vol. xxxix. p. 1848, 1917), but has never been given any quantitative expression. From measurements of the surface-energy changes of a liquid under varied pressures of an adsorbed vapour, the amount of the adsorption might be calculated from the Gibbs equation (*l.c.*), $\Gamma = -\rho \frac{d\sigma}{dp}$, but the actual measurement of the adsorption itself is of much greater difficulty. Very few such measurements are to be found in the literature, the more notable ones being those of Donnan (*Proc. Roy. Soc. A*, vol. lxxxv. p. 558, 1911) and Lewis (*Phil. Mag.* 1908, p. 499, and 1909, p. 466; *Zeit. Phys. Chem.* vol. lxxiii. p. 129, 1910), which were concerned with the adsorption at liquid-gas and liquid-liquid interfaces respectively of substances in solution in the liquid phase. There exist, however, very considerable discrepancies between the experimental values for the adsorption and those calculated with the aid of the Gibbs equation. One reason for this is probably the fact that the substances employed were either electrolytes or organic substances of high molecular weight which tended to form colloidal solutions, and one could not be sure that the gas laws were obeyed with sufficient accuracy, and there was also the difficulty of a probable irreversible gelatinization of the colloid at the interface. The adsorption of a gas or vapour is free from such defects as these, though in the latter case the interesting phenomenon of incipient condensation must not be overlooked.

The first part of this investigation is concerned with a suitable method of measuring the surface tension of a liquid under the prescribed conditions—*i. e.*, a continuously varying vapour phase.

The Drop-weight Method of measuring Surface Tension.

In view of the recent developments of the technique of this method (Harkins and co-workers, *Journ. Amer. Chem. Soc.* vol. xxxviii. p. 839, 1916; vol. xli. p. 499, 1919; vol. xlii. p. 2534, 1920), it was decided to employ it in the preliminary investigations, and, if necessary, to use some

* Communicated by Prof. F. G. Donnan, F.R.S.

other method later as a check on the results. A careful examination, however, of the recent work in this field has convinced the writer that the drop-weight method, though quite satisfactory practically if the procedure of any particular worker be followed rigidly, does not yet rest on a really rational basis. It would seem that as far back as 1881 (Worthington, *Proc. Roy. Soc.* vol. xxxii. p. 362, 1881) and later (Guye and Perrot, *Archives des Sc. Phys.* vol. xi. p. 225, 1901; vol. xv. p. 132, 1903) more was known about the actual conditions of drop formation and detachment than the modern experimenter is aware of, and that in the curious mathematical developments of the original formula much has been assumed but very little explained.

The only reasonable formula for a *cylindrical* drop hanging from a tube under the influence of gravity is the one quoted by Worthington and Lord Rayleigh (*Phil. Mag.* (5) vol. xlviii. p. 321, 1899), namely $w = \pi r T$, where w is the weight of the drop, r the radius of the tube, and T the surface tension. This is an equilibrium condition, and a slight increase in w should result in a detachment of the drop. This, however, never happens, for, by reason of its rapidly changing shape, the drop takes up new positions of equilibrium, and finally detaches at a stage quite beyond our control (Lohnstein, *Ann. Physik*, vol. xx. pp. 237, 606, 1906). The above formula has therefore to be modified by a correction factor, which varies according to the shape of the drop. This is the method that Harkins has adopted in his more recent measurements, but for some reason or other he prefers to use the formula $w = 2\pi r T$; and although this gives correct results in the end, as his method is purely a comparative one, it must be admitted that the whole procedure is far from satisfactory. His definition of an ideal drop, as one conforming to that formula, seems without meaning, and can only be used as a convenient standard for want of a better understanding of the real facts of the case.

There was another formula developed in Worthington's day (Worthington, *l. c.*) which rests on a sounder theoretical basis, and seems to the author to explain in a much more logical manner the more accurate results of the modern experimenter. The fact that it did not come into general use is due to that very reason—that no experimental data in those days were sufficiently accurate to test its validity. Harkins (*l. c.*), for instance, has shown how unsatisfactory were Rayleigh's results, due to the use of thin-walled tubes. The formula is a comparative one, and rested on the assumption at the time, and is certainly in agreement with the

interesting fact at the present day, that different liquids may form drops of similar shape from tubes of different diameters.

If T_1, T_2 be the surface tensions, ρ_1, ρ_2 the densities of two liquids, and K the ratio between two similar linear dimensions of the drops—*e. g.*, the ratio of the radii of the tubes from which they hang, or of the principal radii of curvature,—then the equation of symmetry becomes

$$K^2 = \frac{T_1 \rho_2}{T_2 \rho_1}.$$

A satisfactory proof of this equation has already been given by Worthington, and it will not be necessary to repeat it here; but it will be seen that it affords a most convenient method of calculating the surface tension of any liquid of known surface tension and density. For if, by choosing a suitable radius of tube in both cases, the drops of the two liquids can be made to assume similar shapes, then the value of K , the ratio of the two radii, can be ascertained; and that is all that is required now for the solution of the equation. It is yet to be explained, however, in what way it is possible to ascertain the exact shape of the drop and its variation with the size of the tube employed. Now it is a remarkable fact that the shape of a drop is completely decided by the ratio of the radius of the tube to the radius of the detached portion of liquid considered as a sphere, and although this is purely an experimental fact, there are some theoretical reasons for assuming that this must be the case. If the equation of symmetry is to have any significance at all, it must hold right down to the moment of detachment of the drops; and as the rupture undoubtedly occurs at the point of maximum concavity*, the same fraction of the hanging drop will detach in the two cases; and, moreover, the radii of the spheres which the detached element of fluid immediately forms will bear the same ratio to the radii of the two tubes. Consequently, if we have a small and a large drop, of different liquids but of the same shape, and we imagine them projected on to a screen, both to the same size, then we could not distinguish between the mode of detachment in the two cases, and the projections of the falling spheres would have the same radius.

We have assumed that the rupture occurs at the point of maximum concavity, as it is here that any upward force due to the surface tension is least; and though the cohesive forces of the liquid are now the deciding factors in the detachment,

* Guye and Perrot, *Arch. des Sc. Phys.* vol. xiii. p. 178 (1903).

the fact that these vary from liquid to liquid does not appear to affect the argument. It follows also, from the conditions of symmetry, that the ratio between the distances of these points of maximum concavity from the bases of the drops must have the value K , which is determined entirely by the surface tensions and densities of the liquids forming the drops.

All that is required now is a knowledge of the tube-radius and drop-radius ratio, with a continuously varying radius of tube, for some standard liquid of known surface tension and density.

The most complete and accurate data for this purpose are supplied by Harkins and Brown (Journ. Amer. Chem. Soc. vol. xli. p. 499, 1919), who measured the weights of drops of water falling from tubes of all radii, from 0.09 to 1 cm. The author has calculated the radius of the drop in each case and the ratio it bears to the radius of the tube from which it falls, and the results are given in Table I. and expressed

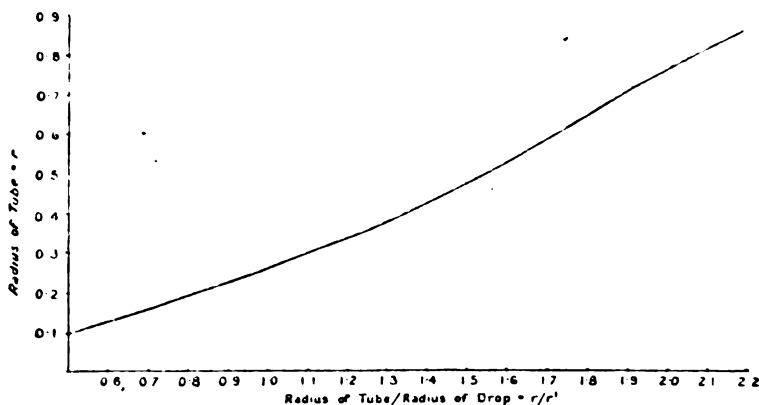
TABLE I.

Radius of tube. r .	Radius of drop. r' .	Ratio. r/r' .
0.09946 cms.	0.1998 cms.	0.4977
0.14769 "	0.2238 "	0.6603
0.19666 "	0.2425 "	0.8112
0.23052 "	0.2532 "	0.9103
0.23790 "	0.2555 "	0.9863
0.26802 "	0.2645 "	1.014
0.27605 "	0.2669 "	1.035
0.29423 "	0.2719 "	1.081
0.29694 "	0.2727 "	1.088
0.31891 "	0.2785 "	1.145
0.32362 "	0.2797 "	1.157
0.34188 "	0.2844 "	1.202
0.37964 "	0.2938 "	1.289
0.39262 "	0.2970 "	1.322
0.44755 "	0.3103 "	1.442
0.50087 "	0.3231 "	1.551
0.55009 "	0.3351 "	1.643
0.59703 "	0.3463 "	1.724
0.65031 "	0.3581 "	1.816
0.69883 "	0.3692 "	1.894
0.72229 "	0.3744 "	1.929
0.74784 "	0.3780 "	1.978
0.77329 "	0.3829 "	2.019
0.79915 "	0.3854 "	2.073
0.84894 "	0.3888 "	2.184
1.0028 "	0.3900 "	2.571

graphically in fig. 1. It will be seen that the ratio varies in a continuous and gradual manner, and passes through unity for one particular radius of tube.

It will be shown now how, with the aid of Table I. and the equation of symmetry, the surface tension of any liquid may be found, provided its density is known. The weight of a drop of the liquid falling from a tube of known radius is first ascertained, from which its radius, and hence the ratio of the tube-radius to the drop-radius, can be calculated. By referring to the table, the radius of the tube corresponding to this ratio in the case of water can be found. In the equation of symmetry the value of K is the ratio of this

Fig. 1.



tube-radius for water to the tube-radius for the other liquid, and since T_1 , ρ_1 the surface tension and density of water, and ρ_2 the density of the liquid are known, its surface tension T_2 is thus easily evaluated. The computation seems a little puzzling at first, but in practice is really very simple and rapid, and gives just as accurate results as any calculation involving the notion of "ideal drops" or the use of various mathematical functions.

To take some concrete cases:—The weight of a drop of mercury falling from a capillary tube, the radius of the bore being 0.0852 cm. (r), was found to be 0.1794 gram at 25° C. The density of mercury at this temperature is 13.53; hence the radius of the drop is 0.1469 cm. (r'): whence $r/r' = 0.5801$. Referring to Table I., we can calculate that, to give this ratio, the radius of the tube for

water must be 0.1239 cm. The value of K is therefore given by $1239/852$, and since $T_1=72.8$, $\rho_1=0.998$, and $\rho_2=13.53$, T_2 has therefore the value 466 dynes per centimetre.

Harkins (*Journ. Amer. Chem. Soc.* vol. xli. p. 513, 1919) gives 0.025783 gram as the weight of a drop of benzene falling at 20°C . from a tube of radius 0.23052 cm. The density of benzene at this temperature is 0.897, and by making a similar calculation the surface tension of benzene is found to be 28.92 dynes per cm. [Richards's (*Journ. Amer. Chem. Soc.* vol. xxxvii. p. 1656, 1915) and Harkins's (*l. c.*) values vary from 28.88 to 28.94 dynes per cm.]

It is essential in all drop-weight determinations that the period of drop formation be fairly long—a matter of minutes,—or that the nearly full-sized drop be allowed to hang for some time, and the detachment effected by very gradual increments of fluid. This is not only to allow sufficient time for surface equilibrium to be reached, especially when we are dealing with a definite adsorption phenomenon, but also to prevent an undue dynamical effect, caused by the too rapid entrance of fluid into the drop. For the same reason, vibration must be avoided as much as possible, as secondary droplet formation might occur and vitiate the results.

It is obvious that this method is applicable to the case of a drop hanging in another liquid of less density than itself; and ρ_2 in the formula becomes then the apparent density of the drop, and the case of a drop detaching upwards in a liquid of greater density than itself could also be catered for by a slight modification of the formula.

The “drop symmetry” method of measuring the surface tension of liquids depends, then, on the conformity of the latter to certain definite principles which, as far as the author is aware, are in the majority of cases followed with remarkable exactness. But it is obvious that liquids of extremely high viscosity, or with a tendency to gelatinize, may have to be excluded from the present considerations; and the difficulty that many of these have in forming drops of definite shape precludes them in any case from all drop-weight methods of measuring surface tension.

The three postulates on which the “drop symmetry” method depends may be re-stated finally as follows:—

- (i.) That it is possible for different liquids to form drops of similar shape when emerging from tubes of different diameters.

- (ii.) That drops of the same shape, which have assumed similar forms continuously to the point of rupture, will detach in similar ways.
- (iii.) That, in the case of all such similar drops, the radius of the tube from which they hang bears a constant ratio to the radius of the detached element of fluid, considered as a sphere.

The principle of symmetry lies at the basis of all comparative drop-weight methods, and, as outlined in the present paper, seems to the author to offer the most satisfactory explanation of the recent accurate experimental results.

Adsorption from the Gas Phase.

This form of adsorption was originally considered by Gibbs (*l. c.*) for the case of mercury and water vapour. Owing to the abrupt change in density of the mercury from the liquid to the gaseous phase, the original equation of equilibrium simplifies to $\Gamma = -\rho \frac{d\sigma}{dp}$, where Γ is the surface excess of adsorbed vapour, ρ the density of the vapour, and $\frac{d\sigma}{dp}$ the rate of change of the surface tension of the mercury with the partial pressure of the vapour. This equation may be deduced in a more simple manner, though by no means as rigidly as in Gibbs's original method, in the following way:—

If we take ν and s as the independent variables defining the system (for a given temperature), and if F denote the thermodynamic potential (ξ function of Gibbs), then

$$\delta F = \nu \delta p + \sigma \delta s,$$

where σ is the interfacial tension.

Hence

$$\left(\frac{\partial \nu}{\partial s} \right)_{p, t} = \left(\frac{\partial \sigma}{\partial p} \right)_{s, t}.$$

But,

$$\rho \delta \nu + \Gamma \delta s = 0,$$

where Γ = excess concentration of vapour per unit area of interface,

and ρ = density of vapour in the vapour phase.

Hence

$$\left(\frac{\partial \nu}{\partial s} \right)_{p, t} = -\frac{\Gamma}{\rho},$$

and therefore

$$\Gamma = -\rho \left(\frac{\partial \sigma}{\partial p} \right)_{s, t}.$$

Adsorption of Organic Vapours by Water.

A number of preliminary experiments have been carried out on the influence of the vapours of certain organic liquids on the surface tension of water.

For this purpose an ordinary dropping pipette was constructed, having a tip made of capillary tube. By means of a constriction in the top of the pipette the drops were made to take at least twenty seconds to form at the tip, and the number obtained from a given volume of water in the pipette, which changed a great deal when the drops were formed in the presence of the vapours, served to indicate the surface tension of the water.

It has been found that the more soluble a substance is in water, the greater is the effect of its vapour on the surface tension of this liquid. Substances such as pentane or hexane, which on shaking with water give solutions having surface tensions very little different from the surface tension of pure water, yield vapours at 20° C. influencing the surface tension to the extent of from 5 to 10 per cent. Substances such as chloroform or methyl acetate have a much greater effect than this, and in addition are much more soluble, their solutions having considerably lower surface tensions than pure water. For the purpose of the present investigation, only substances of very slight solubility could be considered as serviceable, and this seemed to restrict one to the use of the saturated hydrocarbons. As pure specimens of the latter were difficult to obtain, research in this direction has been abandoned for the time being, though it must be admitted that the study of the adsorption of hydrocarbon vapours by water is of peculiar interest and importance, as we are dealing with substances of a non-polar character and anticipate a quite distinct type of adsorption layer.

Adsorption of Organic Vapours by Mercury.

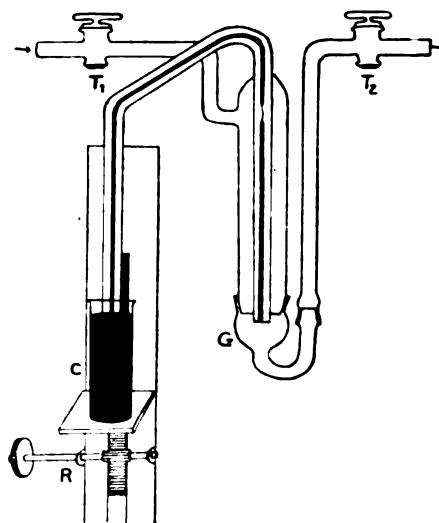
The vapours of all organic liquids seem to have the property of lowering the surface tension of mercury.

In the study of this phenomenon a special apparatus was devised (fig. 2) which, so far, has worked satisfactorily. The dropping pipette consists, as usual, of capillary tube, with a very narrow constriction at one place to slow down the rate of movement of the mercury column, and with a specially prepared tip. This latter was made, as recommended by Harkins (*l. c.*), by filling the capillary with Wood's metal and grinding to a level surface with emery. Rouge was used for the final polishing, and then the Wood's metal

was melted out, and the orifice cleaned with nitric acid and examined under the microscope. For the purpose of accurately measuring the diameter of the orifice a travelling microscope was employed, and a sample of capillary tubing was rejected, in the first instance, if its bore was at all elliptical in cross-section, though it is remarkable that some portions of tubing have so perfectly circular a bore that the slight irregularity, if such exists, is not detectable to within 0.0003 cm. under the microscope.

The rate of formation of the drop is dependent on the difference in height of the orifice of the pipette and the

Fig. 2.—Drop-weight apparatus.



mercury in the container C; and by means of the rack-and-pinion device R, this container can be raised or lowered and the period of drop formation controlled to a nicety. It can be varied from a few seconds to half an hour, and the nearly full-sized drop can be allowed to hang for an even longer period if necessary.

The apparatus was placed in an air thermostat regulated to 0.1 to 0.2 C., and the rack-and-pinion device worked from outside. The air in the thermostat was stirred by means of a fan worked by an electric motor, and although the latter was supported on a framework attached to the wall of the room, some vibration was communicated to the thermostat,

and as a check on the results, the fan was sometimes shut off for a few moments before the drop detached. Slight errors caused by small vibrations are not appreciable; but it may be found necessary, where extremely great accuracy is required, to eliminate even the imperceptibly small vibrations. The drops, as they detached, fell into the removable cup G and were afterwards weighed.

Where it was found necessary to employ a lubricant for the taps, etc., dextrin dissolved in glycerin was used.

In these preliminary experiments, organic vapours mixed with air have been employed. This procedure seems justifiable from certain evidence which will be submitted later.

The vapours were generated by passing a very slow current of dry air at constant pressure through the organic liquids in series of saturators of a type similar to that described by Cumming (*Trans. Faraday Soc.* vol. vi. p. 10, 1910). That efficient saturation was obtained may be judged from the fact that when the temperature of the thermostat was $0^{\circ} \cdot 2$ C. below that of the saturators, visible deposition of liquid occurred on the walls of the glass drop-weight apparatus in the thermostat, and when the temperature of the latter was $0^{\circ} \cdot 2$ C. above that of the saturators no such deposition could be observed.

The following was the procedure adopted in every case:—After the current of vapour had been flowing through the apparatus for some time, the tap T_2 was closed and the current shut off. The vapour in the apparatus was now allowed to acquire the temperature of the thermostat (26° C.), which in some cases was considerably above that of the saturators; but the vapour pressure is decided entirely by the temperature of the liquid in the saturators, and the only difficulty we are concerned with is that the vapour cannot quite reach the temperature of the thermostat while in thermal communication with a portion of its containing vessel at a much lower temperature. This difference, however, was not very great as a rule, and the temperature of the mercury, which is a much better conductor of heat, is really the deciding factor in the adsorption.

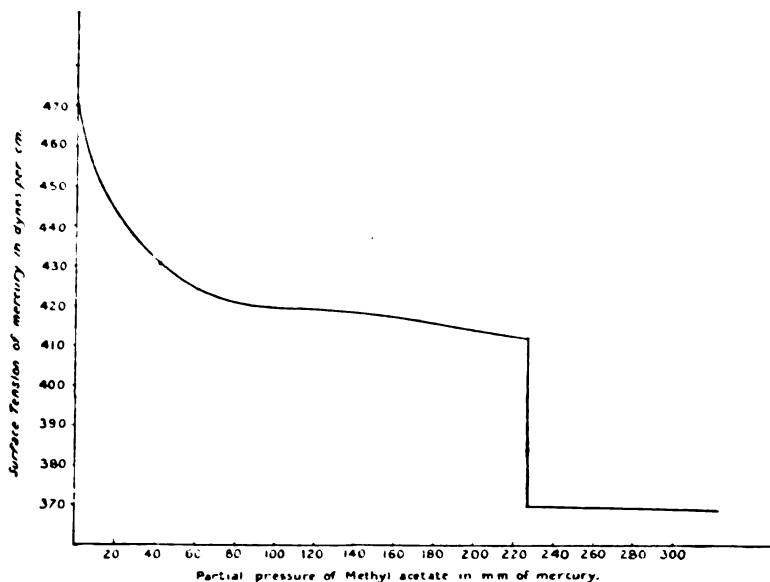
The period of drop formation was never at any time less than three and a half minutes, and with longer periods the weights of the drops were not found to decrease appreciably. The adsorption of the vapour appears, then, to be a fairly rapid process.

The surface tension of mercury in air varies a great deal according to the amount of moisture in the atmosphere. When a current of dry air is passed through the drop-weight

apparatus, as high a value as 472 dynes per cm. has been obtained, which is very little different from the surface tension *in vacuo*.

It was not anticipated, then, that the air present with the organic vapour would interfere very much with the adsorption of the latter. This is an important point, as Stockle's results (Wied. Ann. vol. lxvi. p. 49, 1898) seem to indicate that the presence of air and other gases interferes with the formation of a surface equilibrium with mercury, though only when a dynamical effect is considered. Now that the drop-weight method of measuring surface tension has become practically a statical one, these effects, of course, are not readily observed.

Fig. 3.



The type of curve obtained when the surface tension of mercury is plotted against the varying partial pressures of organic vapour is shown in fig. 3 and is obtained from the data in Table II., the organic liquid in this instance being methyl acetate.

[The mercury was purified by treatment with dilute nitric acid and distillation in a current of air.

The methyl acetate was purified from a commercial sample by treatment with potassium carbonate solution and fractionation after standing over phosphoric oxide.]

TABLE II.

Temperature of saturators.	Vapour pressure of methyl acetate.	Drop weight.	Surface tension of mercury.
—	0 mm.	0.1903 gram.	472 dynes per cm.
-20.0° C.	19 „	0.1780 „	444 „ „
0 „	62 „	0.1685 „	423 „ „
10.8 „	109 „	0.1673 „	419 „ „
15.0 „	137 „	0.1665 „	418 „ „
18.3 „	157 „	0.1658 „	417 „ „
26.0 „	227 „	0.1640 „	412 „ „
	(saturated vapour)	to 0.1454 „	to 370 „ „

(Diameter of orifice of drop-pipette = 0.1796 cm.)

After a certain vapour pressure is reached [the vapour pressures were obtained from Young and Thomas's data (*Journ. Chem. Soc.* vol. lxiii. p. 1209, 1893) for methyl acetate], saturation with an adsorbed film occurs, and the curve becomes practically horizontal. But the phenomenon does not end here. As the temperature of the saturators approaches that of the thermostat, the value of the surface tension suddenly falls; but this seems to depend on certain conditions which are, as yet, outside the control of the experimenter. Two figures are therefore given for the surface tension in the saturated vapour: the highest obtainable, which is near the value for the saturated adsorption; and the lowest, which is practically the value of the surface tension of mercury in liquid methyl acetate. The rest of the curve is hypothetical, and merely indicates that the surface tension at the interface of the two liquids considered does not alter much with increased pressure. This makes up the complete form of the curve, but the most interesting parts of it are the first three—namely, a phase of increasing adsorption, a saturation phase, and a condensation phase.

A calculation from the formula $\Gamma = -\rho \frac{d\sigma}{dp}$ of the adsorption for a vapour pressure of 62 mm. leads to a value for Γ of about 4.5×10^{-8} gram of methyl acetate per square centimetre. It can be further calculated from this result that the number of methyl-acetate molecules per square centimetre of mercury surface is 0.37×10^{15} . It seems, then, that in all probability we have a monomolecular layer, as this figure is very near the values given by Langmuir (*Journ. Amer. Chem. Soc.* vol. xxxviii. p. 2288, 1916) for monomolecular layers of carbon dioxide, nitrogen, etc.

Moreover, the space taken up by each molecule (27×10^{-16} sq. cm.) is near that required for molecules of esters and fatty acids on the surface of water, namely 23×10^{-16} sq. cm., and it is possible that the same type of orientation obtains on the mercury surface.

There appears, however, to be a somewhat abrupt change from a simple adsorption process to a condensation, and this phenomenon is now being investigated in greater detail.

I am indebted to Professor Donnan for suggesting to me the idea of this research and for the great interest he has taken in its progress, and to the Royal Commissioners of the 1851 Exhibition for a scholarship which is enabling me to continue the work.

Physico-Chemical Laboratory,
University College, London,
March 20, 1923.

CXIII. *Notices respecting New Books.*

Prolegomena to Analytical Geometry in Anisotropic Euclidean Space of Three Dimensions. By ERIC HAROLD NEVILLE, late Fellow of Trinity College, Cambridge and Professor of Mathematics in University College, Reading. Cambridge University Press, 1922. 30s. net.

IN a stimulating volume, Professor Neville has given an account of the principles underlying the use of Cartesian axes and vector frames in ordinary space and of ideal complex Euclidean space of three dimensions. In the first section the Author deals with various fundamental matters such as, for example, attaching signs to the volume of a tetrahedron, matters in the discussion of which it is of great importance to avoid ambiguity. The next section is concerned with vector analysis and gives an account of the development of the subject. The exposition is very clear, and the logical status and the characteristics of a vector—a complex in which a number is associated with a direction—are developed in a manner which, quite apart from the uses to which the theory of vectors is put in subsequent sections of the volume, is of great value in that it affords an admirable example of the modern logical method in mathematics which was introduced by Frege and Russell. The next section applies vector analysis to obtain formulæ for use with Cartesian axes and with vector frames; the next deals with the construction of algebraic space, and the final section with ideal space.

There are two aspects from which the present volume might be discussed. As regards the actual progress of geometry, it is evidently of great importance that the attention of students of geometry should be directed towards the problems which are here

discussed. Quite apart from the particular treatment accorded to them in this book, it is of real value to have the problems stated clearly and incisively.

On the other hand, the careful study of this book will repay students of mathematics who wish to understand something about the structure of mathematics. The method of definition and the logical development of the characteristics of vectors adopted here show clearly the kind of way in which any body of mathematical knowledge must finally be built up. The building-up of any domain of knowledge can, of course, only come after the new ideas have been conceived and the discoveries have been made. Once the material exists, even if it exists only in the form of isolated results, the building-up of the results into a new domain of knowledge can only be accomplished by the careful critical development of the characteristics of concepts defined in abstract terms. The present work enables us to see this building process in operation. As an example of the logical method at its best, Professor Neville's work can be enthusiastically recommended.

D. M. W.

British (Terra Nova) Antarctic Expedition 1910-1913. I. *Determinations of Gravity*: 4to, pp. 105+plates 4; 7s. 6d. net.
II. *Observations on the Aurora*: 4to, pp. 46+plates 2; 7s. 6d. net. By Capt. C. S. WRIGHT. Harrison & Sons.

THE first of these papers is an account of the determination of the value of gravity at Cape Evans during the last Scott Antarctic Expedition. It deals mostly with the experimental methods employed. The result is that the value of gravity at Cape Evans, 10 feet above sea-level, is $983\cdot003 \pm \cdot002$ cm/sec². The observations seem to have been carried out with remarkable care and precision in the difficult circumstances. To indicate the kind of difficulties that had to be faced, one may mention that hoar frost, largely from the observer's breath, was formed on the optical parts of the apparatus, and the temperature was so low that a wait of about two weeks was necessary for this to evaporate. On the other hand, the low temperature was found useful in the construction of a support for the pendulums: the freezing of water in the interstices of gravel produced a quite satisfactory concrete. The result will be of much use in investigations of the figure of the earth: observations at more stations would, of course, be required before we could reach any conclusion about the isostatic compensation of the Antarctic Continent. Other determinations were made at Christchurch, Wellington, and Melbourne, and the whole checked against Potsdam.

The auroral observations were made at Cape Evans and Cape Adene, and have been analysed with regard to the diurnal variation and the relation to terrestrial magnetism. They cannot be discussed satisfactorily in a short abstract; the paper will be a valuable source of information to investigators of polar phenomena.

H. J.

Tables Annuelles Internationales de Constantes et Données Numériques de Chimie, de Physique et de Technologie. Vol. IV. Parts 1 and 2 (2 volumes). Gauthier-Villars (Paris); Cambridge University Press (Cambridge); University of Chicago Press (Chicago), 1922.

THE publication of these valuable tables was interrupted by the war. The two volumes now issued are evidence of the great effort which is being made to deal effectively with the vast mass of material which has accumulated since the appearance of the last volume in 1914. They cover the years 1913 to 1916 inclusively; Volume V., which is announced to be in preparation, will carry the work up to the end of 1920.

Wherever we have consulted the tables, we have found them very complete as far as the period covered is concerned. The arrangement, however, still leaves something to be desired: for instance, data covering the X-ray spectra are to be found in Part 1 under the general heading *Spectres d'émission*, subheading *Emissions de rayons X*, and different data for the same period in Part 2 under the heading *Rayons Roentgen*, subheading *Spectres de rayons Roentgen*. This particular case is not of great practical importance, because all workers are aware that the data given have by now been mostly superseded by more refined measurements, but it indicates a need of more careful classification. It is, however, ungracious to find minor faults in a performance of such difficulty as the assemblage and arrangement of these masses of tables at the present time. To get some idea of the labour involved, it is only necessary to glance at, say, the section dealing with magnetism. We feel that all physicists will congratulate M. Marie, the general secretary, and his collaborators on the appearance of these volumes, and do their best to give what help they can to promote the speedy appearance of Volume V. All communications on the subject of the tables are welcomed by the secretary.

We would like to suggest that it would be acceptable to working physicists if the latest values of all the universal constants could be assembled together, instead of being scattered under various headings.

X Rays. By G. W. C. KAYE. Fourth Edition. Longmans, 1923. Price 16s.

DR. KAYE's excellent little book, dealing in an elementary manner with all aspects of X rays, has now gone into a fourth edition. There have been no essential changes made, but fresh matter has been added on the practical uses of X rays, including both the industrial applications and the work done on old pictures by Drs. Heilbron and Chéron, in which advantage is taken of the different X-ray absorption of different pigment layers to reveal details which have been painted over. The only criticism which

we have to offer of the new edition does not affect Dr. Kaye: it is that, in spite of the much enhanced price, the book is not so well produced as was the first edition.

The Principle of Relativity with applications to Physical Science. By A. N. WHITEHEAD. Cambridge University Press. Price 10s. 6d.

PROFESSOR WHITEHEAD in this volume has put forward an alternative rendering of the Theory of Relativity which calls for careful and thorough examination.

The first part deals with general principles of a philosophical nature. It carries a good deal further the inquiry undertaken by the author in his two previous works 'The Principles of Natural Knowledge' and 'The Concept of Nature,' and it should be read in connexion with them. In this discussion of the character of our knowledge in general and of our knowledge of nature in particular, the author comes to the conclusion that our experience exhibits and requires a basis of uniformity—a uniformity which in the case of nature exhibits itself in the uniformity of spatio-temporal relations. This conclusion is in severe disagreement with the spirit of Einstein's second theory, and Professor Whitehead's searching analysis and detailed working-out of his own point of view which is grounded in these philosophical premisses is consequently of the greatest interest. A second fundamental divergence from conventional Relativity is to be found in the view of the inter-relation of physics and geometry which is here expounded. One of the most novel parts of the theories of Einstein is the suggestion that different types of geometry can be made to absorb different types of physical force. The large step from the first theory of Relativity of 1905 to the second of 1915 consists largely in the suggestion that a certain specific type of geometry can be made to absorb gravitational fields. In the present volume, however, a very different view is taken. Physics and Geometry are considered to be fundamentally distinct. The point of view adopted is developed with the admirable logical skill always to be found exhibited in the works of the author from premisses suggested by general philosophical considerations.

These important divergences from orthodox Relativity theory as it has grown up during the last eight years call for detailed consideration. The great skill of the author as a mathematician and a logician, and in particular as a Geometer, make this book an important challenge to Relativists in general. It is unnecessary to describe the method of treatment of the present volume otherwise than by referring to the author's international reputation as a keen thinker whose splendid work in these domains has done much to initiate a new epoch in the logic of science.

CXIV. *Intelligence and Miscellaneous Articles.*

THE REACTION CONSEQUENT UPON THE EVAPORATION OF A LIQUID AND UPON THE EMISSION OF VAPOURS FROM SMALL ORIFICES.

[The following addition to Professor Duffield's paper under the above title reached us after our April number was published. It should be added at the end of Section 4 on p. 676.—Eds.]

WE may, I think, obtain some indirect evidence concerning the rate at which the molecules of a vapour issue from a boiling liquid, from a series of observations made by Royds (Phil. Trans. Roy. Soc. A, 1908) upon the mechanism of the electric spark. Using a method devised by Schuster and Hemsalech, he photographed the spectrum of the spark upon a rapidly-moving film and obtained lines drawn out into streamers, whose inclination gave a measure of the velocity of the material in terms of the velocity of the film. In all cases they were greatest close to the pole; the maximum velocities measured may be taken as approximating to the velocities of projection.

In the accompanying table we compare these velocities, $v_{obs.}$, with those of atomic agitation, v_T , of the material of the poles, on the assumption that the temperature, T , of the hot pole is that of the boiling-point, as it almost certainly is in the arc. For this purpose we use the equation $v_T = v_H \times \sqrt{2.273 \times \sqrt{T}/M}$, where v_H is the velocity of the hydrogen molecule (18.39×10^4 cm./sec.) and M is the atomic weight of the material. We see from the table that the two velocities are of the same order of magnitude; indeed, considering the difficulties in the measurements, the agreement is remarkable. In some cases two types of lines were distinguished by Royds, and designated by him Types I. and II.; usually the former give velocities rather less, and the latter velocities greater than v_T . Royds regards the streamers as being charged negatively, but I think the only evidence in favour of this is that they seem to emanate from the pole which is momentarily the cathode; it may, however, well be that only the cathode is raised to the boiling-point. Since the velocities fall off as the vapour reaches the centre of the gap, it is clear that the atoms are *projected*: they do not start from rest and accelerate under the forces of the field, but rather diffuse into the surrounding vapour. There is some reason for thinking that the streamers are rendered visible by fast-moving electrons projected from the cathode at the same time that the vapour is emitted.

Taking the agreement between calculated and observed values of the velocities in conjunction with other indications, the view is strengthened that molecules are projected from a boiling liquid with their temperature velocities.

Element	Mg.	Al.	Zn.	Cd.	Sn.	Sb.	Hg.		Pb.		Bi.	
Type	I.	II.	I.	I.	II.	II.	—	—	I.	II.	I.	II.
Velocity obs., $v_{obs.}$...	4.6	8.7	3.9	4.0	13.7	22.3	9.4	11.5	3.0	19.6	2.8	20.2
.. calc., v_T	11.9	13.7	6.7	4.8	7.2	5.9	2.8	2.8	3.6	3.6	4.5	4.5
Ratio, $v_T/v_{obs.}$	2.6	1.6	1.7	1.2	.5	.3	.3	.3	1.2	.2	1.0	.2

FIG. 8.

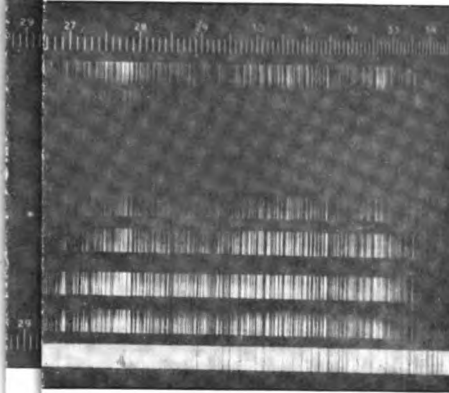


FIG. 1.

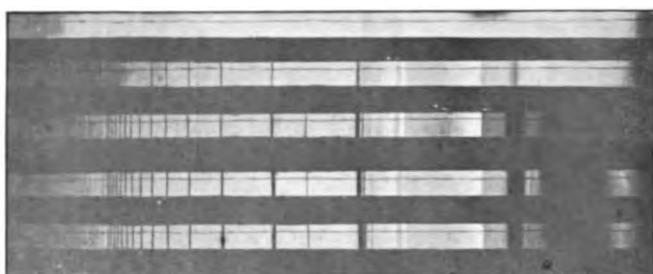
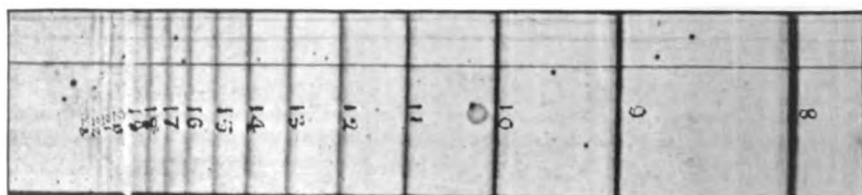


FIG. 2.

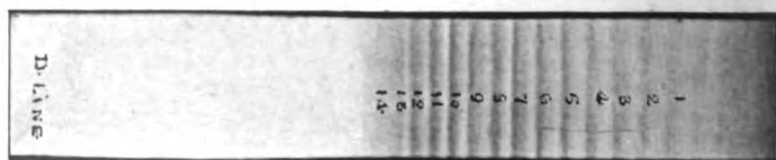


FIG. 3.



Enlarged photograph of a section of Fig. 2.

FIG. 5.



Channelled Spectrum.

FIG. 4.

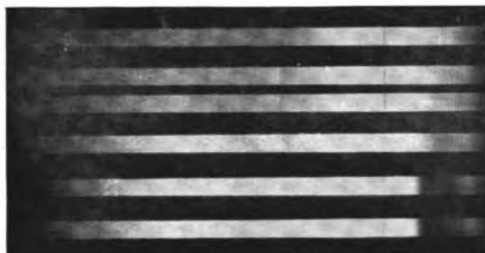
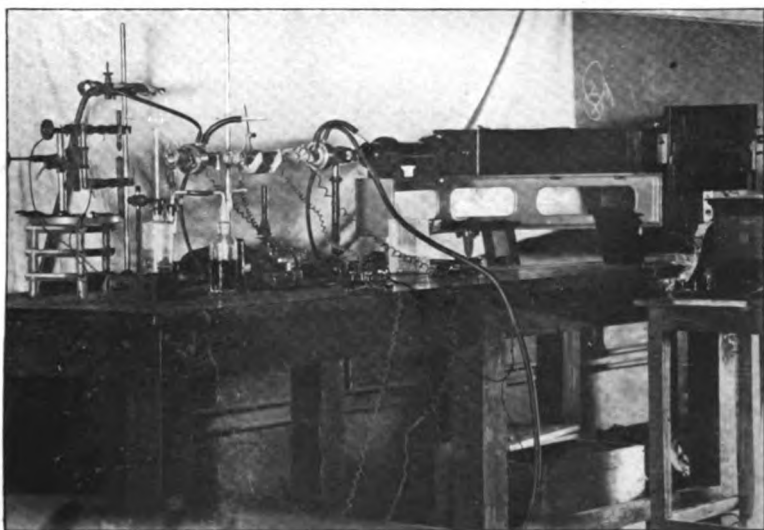
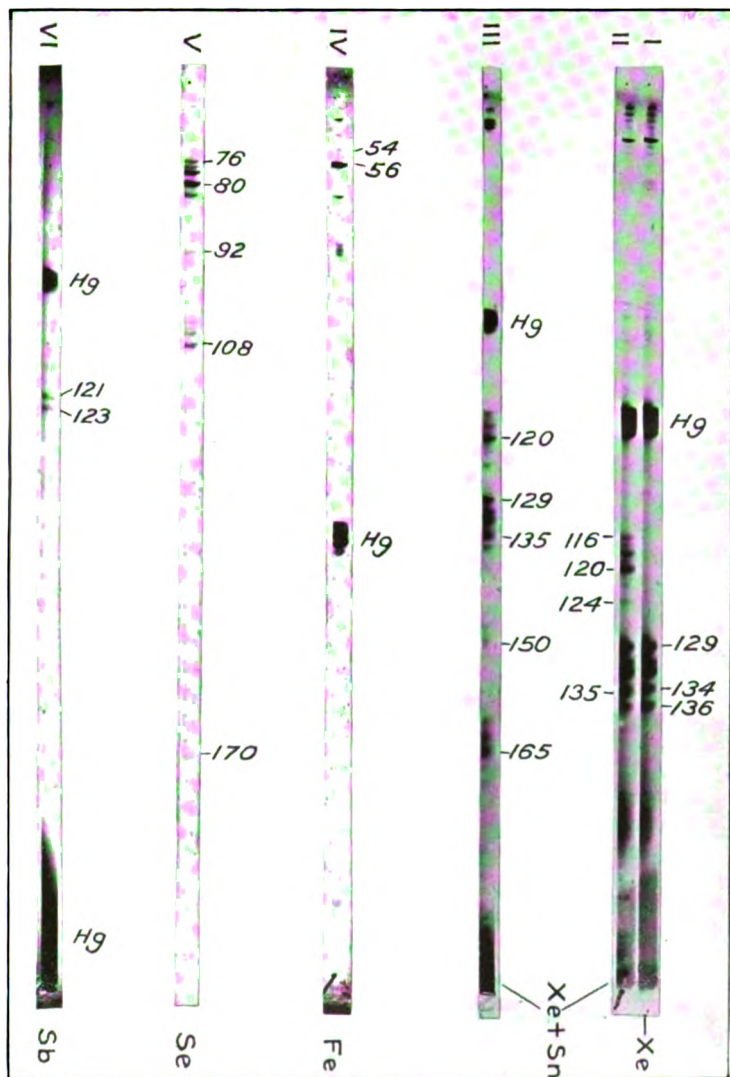
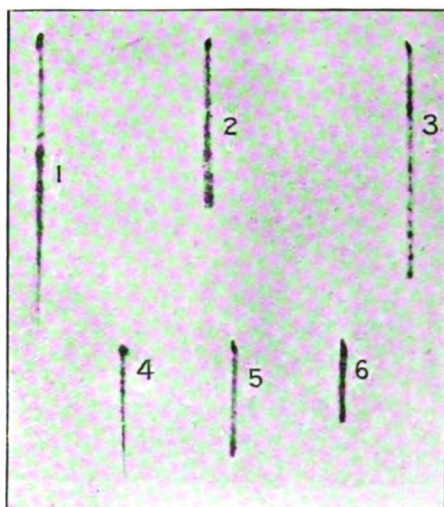


FIG. 6.



Apparatus as it stood in our study of the absorption of K-vapour.





The rest atom tracks all point upwards.

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

JUNE 1923.

CXV. *The Electronic Theory of Valency.*—I. *Intramolecular Ionization.* By THOMAS MARTIN LOWRY*.

I. *Introductory.*

THE theory of intramolecular ionization was put forward in 1914 by Sir Joseph Thomson in a paper on "The Forces between Atoms and Chemical Affinity" (*Phil. Mag.* [6] xxvii. p. 757, 1914). It was based on phenomena observed with positive rays, where it was found that negatively- as well as positively-charged atoms of hydrogen, oxygen, carbon, and chlorine were present in the discharge. These must obviously have taken up at least two electrons in order to neutralize and then to reverse the positive charge with the help of which they were driven through the cathode. Opposite polarities were shown, therefore, to be possible in the atoms of many of the common elements, and it was suggested that this might also occur under more commonplace conditions.

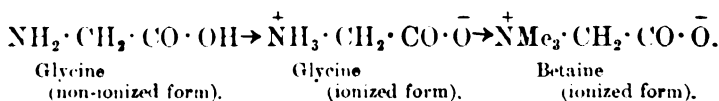
Since it appeared that ionized molecules would have a greater electrical moment than those which were neutral throughout, it was possible in the case of gases to apply experimental tests in order to determine whether internal ionization had or had not taken place. A number of common

* Communicated by the Faraday Society.

gases were therefore classified, with the help of observations on specific inductive capacity and refractive index, into two groups, as follows :—

Group I. *Not Ionized.* $H_2, O_2, N_2, Cl_2,$ $He, CO, CO_2, CS_2,$ $CH_4, CCl_4, C_6H_6, N_2O.$ Group II. *Ionized.* $HCl, CH_3Cl, CHCl_3$ (weak), $H_2O, CH_3 \cdot OH, C_2H_5 \cdot OH,$ $NH_3, SO_2.$

To chemists, intramolecular ionization is most familiar in the case of the organic amino-acids, such as glycine, the salt-like formula for which is justified by the conversion of glycine on methylation into betaine, which cannot pass into a non-ionized form except by addition of water.



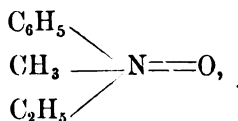
The introduction of electronic formulæ based on the theory of octets has, however, made it necessary to postulate a condition of intramolecular ionization in a large number of compounds where nothing of the sort has been suspected previously. Thus, in the two isosteric gases, carbon dioxide and nitrous oxide, the nuclear charges and the attached electrons are found to be perfectly balanced in carbon dioxide, which Lewis represents as $:\ddot{O}::C::\ddot{O}:$, if each electron that is shared with another atom is reckoned as one-half; but in nitrous oxide, $:\ddot{O}::N::\ddot{N}:$, where the nuclear charges are $8+7+7$ instead of $8+6+8$, this balance is destroyed by the transfer of a unit of positive electricity from the nucleus of one of the outer atoms to the nucleus of the central atom of the chain. If carbon dioxide be written as $O=C=O$, nitrous oxide must then be written

as $O=\overset{+}{N}=\bar{N}$, or $O=N\equiv N$, where the barb represents an electrovalency directed from the + to the - atom. In addition to its application in organic chemistry, which will form the subject of another paper, the theory of intramolecular ionization has a number of applications in inorganic chemistry, and these are set out briefly in the paragraphs which follow.

2. Odd and Even Valencies.

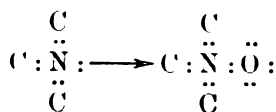
Before the advent of the octet theory, chemists were wont to divide the elements into two groups according as the typical valencies were odd or even numbers. This subdivision was based on a rule, to which there are not many exceptions, that when the valency of an element varies, it generally increases or diminishes by two units. The principal exceptions to this rule are found in nitric oxide, NO, nitrogen dioxide, NO₂, triphenylmethyl, C(C₆H₅)₃, and in certain cases of dissociation such as monatomic iodine, where, as Lewis points out, the total number of electrons in the molecule is an odd number. With the advent of the octet theory, it appeared that each element had, as a rule, only one principal valency, although electro-negative elements could use this either as a covalency or as an electrovalency of equal number; apart from this exception, it looked as if every case of variable valency represented an exception to the general rules of the octet theory. When, however, the possibility of "mixed" bonds is admitted, it is seen that in a large number of cases *two* units of valency may be added, namely one covalency and one electrovalency, without disturbing the arrangement of the octets on which the primary valency was based; these cases will be found to cover nearly all the instances in which Langmuir has used variable valencies in constructing electronic formulæ for inorganic compounds (J. Amer. Chem. Soc. xli. p. 868, 1919).

This effect can be demonstrated most easily in the case of oxygen, which has six electrons in its outer shell. Since a single octet contains eight and a double octet contains fourteen electrons in the outer shell, an atom of oxygen can, if other conditions are favourable, be added to any saturated octet which is not already surrounded by four other atoms or radicles. This limitation makes it impossible to increase the valency of carbon from 4 to 6 by converting methane into an oxide, since all the electrons of the octet have already been converted into duplets; but, in the case of nitrogen, saturated compounds of the ammonia-type can be converted into oxides, as in the case of the methylethylaniline oxide,

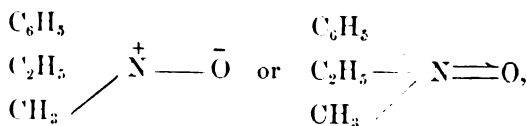


which was prepared by Meisenheimer in optically active
4 B 2

forms. From the point of view of the octet theory, the oxidation of the nitrogen atom in methylethylaniline is represented by the scheme

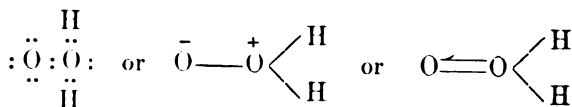


This shows the last available edge of the nitrogen octet as being gripped by an oxygen atom, $\ddot{\text{O}}:$, which carries with it the six electrons that are needed to add an additional octet to the system. Langmuir (J. Amer. Chem. Soc. lxii, p. 280, 1920) states definitely that in this compound "the nitrogen is quadricovalent, and it is entirely unnecessary to assume a quinquivalent nitrogen." It is difficult to believe that Langmuir can have overlooked the fact that in this system the nitrogen atom is positively charged (and thereby converted into a kation), whilst the oxygen is negatively charged, and so converted into a "bound" anion, since the two ions are united by the covalency as well as by the electrovalency; but I cannot find in any of Langmuir's papers a clear recognition of the phenomena of intramolecular ionization, or of the existence in this compound of "bound" ions corresponding with the "free" ions of ammonium chloride. It therefore really looks as if the obvious method of representing this compound as one in which the oxygen is linked to the nitrogen by a mixed double bond, including one covalency and one electrovalency, thus



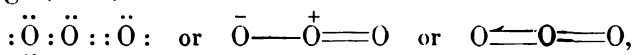
may perhaps be novel.

By bracketing the oxygen atom in a precisely similar way onto a molecule of water, a formula is obtained in which the valency of one atom of oxygen is increased from 2 to 4 just as that of the nitrogen was increased from 3 to 5 by converting methylethylaniline into its oxide. The formulæ



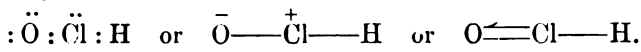
appear to represent the properties of free hydrogen peroxide

more accurately than the conventional formula which shows the compound as containing two hydroxyl groups linked by a covalency, thus $\text{HO} \cdot \text{OH}$. Its close resemblance to ozone may be shown by representing the latter compound as one in which an oxygen atom is bracketed onto a molecule of oxygen, thus,

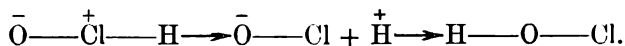


the valency of one of the oxygen atoms being again increased by two units, one of covalency and one of electrovalency.

Theoretically it should be possible to treat hydrogen chloride in the same way and to convert it into an oxy-acid in which the valency of the chlorine would be raised from 1 to 3 by the addition of one unit of covalency and one of electrovalency, thus,



In practice, however, it is clear that the ionization of this molecule would leave the anion with a negative charge on the oxygen, and that the hydrogen ion would therefore be likely to return to the oxygen rather than to the uncharged chlorine.



The formula for hypochlorous acid in its non-ionized form is therefore not $\text{H}-\text{Cl}=\text{O}$ but $\text{H}-\text{O}-\text{Cl}$, and it is from this latter compound that any scheme for increasing the valency of chlorine in this series of acids must start. In the ion, however, as will be shown below, there is nothing to distinguish this first atom of oxygen from those which are introduced subsequently.

3. Stability of Oxy-acids.

The increasing stability of the oxy-acids and of their salts as the number of oxygen atoms increases appears to receive a clearer explanation than has hitherto been possible now that the phenomena can be interpreted in the light of the phenomenon of intramolecular ionization.

(a) *Oxy-acids of Chlorine.*—The complete series of chloro-acids may be set out as in Table I., which shows in the case of each ion (i.) the ordinary chemical formula, (ii.) the electronic formula, (iii.) the electronic formulæ interpreted by means of the theory of intramolecular ionization, (iv.) an

alternative representation of the mixed double bonds in which the total number of valencies can be seen more clearly than when + and - signs are used.

TABLE I.

Electronic Formulæ for the Ions of the Chloro-acids.

Name of acid.	Formula of Ion.	Electronic Formula of Ion.	Formulæ showing Mixed double Bonds.
Hydrochloric acid...	Cl'	$\ddot{\text{Cl}}:$	$\bar{\text{Cl}}$
Hypochlorous acid..	ClO'	$\ddot{\text{Cl}}:\ddot{\text{O}}:$	$\text{Cl}-\bar{\text{O}}$
Chlorous acid	ClO ₂ '	$\ddot{\text{O}}:\ddot{\text{Cl}}:\ddot{\text{O}}:$	$\bar{\text{O}}-\overset{+}{\text{Cl}}-\bar{\text{O}}$ or $\text{O}=\text{Cl}=\text{O}$
Chloric acid	ClO ₃ '	$\begin{array}{c} \ddot{\text{O}}: \\ \ddot{\text{O}}:\ddot{\text{Cl}}:\ddot{\text{O}}: \end{array}$	$\begin{array}{c} \bar{\text{O}} \\ \\ \bar{\text{O}}-\overset{++}{\text{Cl}}-\bar{\text{O}} \end{array}$ or $\begin{array}{c} \text{O} \\ \\ \text{O}=\text{Cl}=\text{O} \end{array}$
Perchloric acid	ClO ₄ '	$\begin{array}{c} \ddot{\text{O}}: \\ \ddot{\text{O}}:\ddot{\text{Cl}}:\ddot{\text{O}}: \\ \ddot{\text{O}}: \end{array}$	$\begin{array}{c} \bar{\text{O}} \\ \\ \bar{\text{O}}-\overset{+++}{\text{Cl}}-\bar{\text{O}} \\ \\ \bar{\text{O}} \end{array}$ or $\begin{array}{c} \text{O} \\ \\ \text{O}=\text{Cl}=\text{O} \\ \\ \text{O} \end{array}$

The most conspicuous feature of the formulæ in the fourth column is the progressive growth of the positive charge on the chlorine atom. This atom is originally negative, but passes through the successive stages of $\overset{+}{\text{Cl}}$, $\overset{++}{\text{Cl}}$, $\overset{+++}{\text{Cl}}$ until it carries a surplus of three positive charges. Since the oxygen in each of these compounds is negatively charged, it is clear that the stability of the oxy-acids should increase as the polarity of the central-chlorine atom increases. A maximum is, however, reached in the case of perchloric acid because all the electrons of the chlorine octet are now shared with other atoms and no more oxygen atoms can be bracketed onto the chlorine.

(b) *Oxy-acids of Sulphur.*

In the case of the sulphur-acids, it is interesting to note

TABLE II.

Electronic Formulæ for the Ions of the Sulphur-acids.

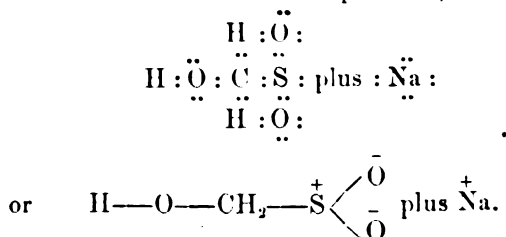
Name of acid.	Formula of Ion.	Electronic Formula of Ion.	Formula showing Mixed Double Bonds.
Sulphuretted hydrogen	S ^{''}	$\ddot{\text{S}}:$	$\overline{\text{S}}$
H ₂ SO (not known) ...	SO ^{''}	$\ddot{\text{S}}:\ddot{\text{O}}:$	$\overline{\text{S}}-\overline{\text{O}}$
H ₂ SO ₂ (not known) ...	SO ₂ ^{''}	$\ddot{\text{O}}:\ddot{\text{S}}:\ddot{\text{O}}:$	$\overline{\text{O}}-\overline{\text{S}}-\overline{\text{O}}$
Sulphurous acid	SO ₃ ^{''}	$\ddot{\text{O}}:$ $\ddot{\text{O}}:\ddot{\text{S}}:\ddot{\text{O}}:$	$\begin{array}{c} \overline{\text{O}} \\ \\ \overline{\text{O}}-\text{S}^+-\overline{\text{O}} \end{array}$ or $\text{O} \begin{array}{c} \updownarrow \\ \text{S} \\ \updownarrow \end{array} \text{O}$
Sulphuric acid	SO ₄ ^{''}	$\ddot{\text{O}}:$ $\ddot{\text{O}}:\ddot{\text{S}}:\ddot{\text{O}}:$ $\ddot{\text{O}}:$	$\begin{array}{c} \overline{\text{O}} \\ \\ \text{O}-\text{S}^{++}-\text{O} \\ \\ \overline{\text{O}} \end{array}$ or $\text{O} \begin{array}{c} \updownarrow \\ \text{S} \\ \updownarrow \end{array} \text{O}$

that the double negative charge of the sulphide ion, $\overline{\text{S}}$, would be distributed between sulphur and oxygen in the ion of the hypothetical acid, H₂SO, whilst the ion of the acid, H₂SO₂, has both negative charges on oxygen and none on sulphur. Under these conditions, it is not surprising to find that the acid, H₂SO, the ion of which would consist of two negatively-charged atoms, appears not to be capable of existence, whilst the ion, SO₂, which would have two negatively-charged atoms of oxygen attached to a neutral atom of sulphur, is apparently of the same low order of stability as the ion ClO', where precisely similar conditions prevail. Stable ions only begin to be formed when the central sulphur atom acquires a positive charge as in the ions of the sul-

phites $\begin{array}{c} \overline{\text{O}} \\ \diagup \quad \diagdown \\ \overline{\text{O}} \end{array} > \text{S}^+-\overline{\text{O}}$ and sulphates $\begin{array}{c} \overline{\text{O}} \\ \diagup \quad \diagdown \\ \overline{\text{O}} \end{array} > \text{S}^{++} < \begin{array}{c} \overline{\text{O}} \\ \diagup \quad \diagdown \\ \overline{\text{O}} \end{array}$. In this

connexion it is of interest to note that the acid, H₂SO₃, (which is the only one to which the name of hypsulphurous

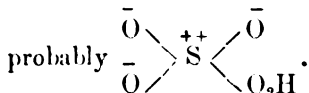
acid can be correctly applied *), although itself unknown, is manufactured on a large scale as a commercial reducing agent in the form of a condensation-product with formaldehyde, sodium formaldehyde sulphonylate, $\text{HO}\cdot\text{CH}_2\cdot\text{SO}\cdot\text{ONa}$. The electronic formula of this compound is, however,



The electronic formula shows clearly that in this case also stability is only achieved when the sulphur atom has acquired a positive charge. This has, in fact, been done by treating the acid as monobasic, with one hydrogen atom attached directly to sulphur instead of through oxygen; the electronic formula of the hypothetical mono-sodium salt would then be $\ddot{\text{O}} : \ddot{\text{S}} : \ddot{\text{O}} : \text{plus} : \ddot{\text{Na}} :$ or $\bar{\text{O}}-\overset{+}{\text{S}}\text{H}-\bar{\text{O}} \text{ plus } \overset{+}{\text{Na}},$
H

and the sulphur atom is again seen to be carrying a positive charge.

The sulphur-series of oxy-acids again stops short at a point where four oxygen atoms are linked to the central atom. A persulphuric acid of the formula H_2SO_6 is indeed known, but it is a monobasic acid, which must be formulated as a monosulphonic derivative of hydrogen peroxide, and its ion is



* Ordinary "hypo" was at first thought to be a real hyposulphate having the formula NaHSO_3 , in which one of the molecules of water of crystallization was taken into the structure ($\text{Na}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O} = 2\text{NaHSO}_3$); it is, however, derived from a dibasic acid of the S_2 series, and its ion

is formulated as $\text{SO}_3\text{O}_2 = \begin{array}{c} \bar{\text{S}} \\ \diagup \\ \bar{\text{O}} \end{array} \text{S}^{++} \begin{array}{c} \diagdown \\ \bar{\text{O}} \end{array}.$ Zinc hydrosulphite, which is

also sometimes called a hyposulphite, was thought to be ZnSO_2 instead of ZnS_2O_4 ; this salt, is, however, also derived from a dibasic acid of the

S_2 series, and its ion is formulated as $\begin{array}{c} \bar{\text{O}} \\ \diagup \\ \bar{\text{O}} \end{array} \text{S}-\text{S} \begin{array}{c} \diagdown \\ \bar{\text{O}} \end{array}.$ It will be noticed that the ions of these stable compounds have, like those of the sulphites and sulphates, a positive charge on the central sulphur atoms.

(c) *Oxy-acids of Phosphorus*.—The most stable acid of phosphorus is again the one which contains four oxygen

atoms. Its ion PO_4''' may be written as $\begin{array}{c} \bar{\text{O}} > \text{P}^+ < \bar{\text{O}} \\ \bar{\text{O}} < \end{array}$,

where it is seen that the atom of phosphorus carries only a single positive charge. The corresponding acid with three atoms of oxygen would therefore have a neutral atom in the

centre of three negatively-charged oxygens $\begin{array}{c} \bar{\text{O}} > \text{P} \\ \bar{\text{O}} < \end{array} \text{—}\bar{\text{O}}$,

and would be of very low stability: actually, however,

phosphorous acid is only dibasic, and its ion $\begin{array}{c} \text{H} > \text{P}^+ < \bar{\text{O}} \\ \bar{\text{O}} < \end{array}$

retains a single positive charge, very much as in the case of the sulphylic acid, quoted under (b) above. The next acid of the series, hypophosphorous acid, H_3PO_2 , behaves in a corresponding way, since this is only monobasic; its ion,

$\begin{array}{c} \text{H} > \text{P}^+ < \bar{\text{O}} \\ \text{H} < \end{array}$, therefore still retains the single positive charge,

which appears to be essential for stability in nearly all the oxy-acids.

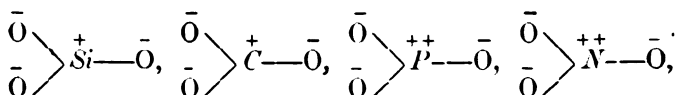
(d) *Silicic Acid*.—In the case of silicon, even the O_4 acid has a neutral atom in the centre of the ion SiO_4''' , which

must be represented as $\begin{array}{c} \bar{\text{O}} > \text{Si} < \bar{\text{O}} \\ \bar{\text{O}} < \end{array}$. Less highly oxy-

genated acids of which the ions would contain a negatively-charged silicon atom surrounded by negatively-charged oxygen atoms are unknown.

(e) *Dehydrated Acids*.—In all the above cases the formulæ assigned to the various ions agree, so far as covalencies are concerned, with the formulæ attributed to them by Langmuir; but as he failed to recognise the intramolecular ionization of these compounds, and therefore omits all the charges on the atoms, it was not possible for him to arrive at the simple theory set out above, that stability in oxy-acids usually depends on retaining a positive charge on the central

atom, without which it is difficult to hold the negatively-charged oxygen atoms. In the case of the dehydrated acids such as H_2SiO_3 and H_2CO_3 , or HPO_3 and HNO_3 , which are derived from acids of the O_4 series by the removal of water, satisfactory formulæ are provided most readily by assigning to the central atom a "sextet" (Lewis, J. Amer. Chem. Soc. xxxviii. p. 775, 1916; Latimer & Rodebush, *ibid.* lxii. p. 1429, 1920) or "depleted octet" of 8 or 16 electrons instead of the $2+8$ or $2+8+8$ electrons of the normal octet. The introduction of this conception has very far-reaching consequences in organic chemistry, and its introduction in inorganic chemistry appears, therefore, to be at least worthy of a trial. On this basis the ions of the four acids cited above become



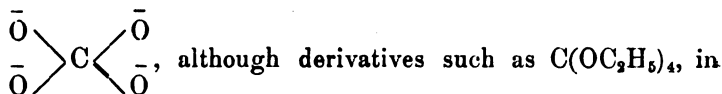
where the symbols printed in italics are those of atoms which are assumed to carry two electrons less than the usual number; the much greater stability of the O_4 acids of silicon and phosphorus as compared with carbon and nitrogen may perhaps be associated with the greater difficulty of carrying out this robbery in the case of atoms containing three shells of electrons instead of two. The new formulæ have the advantage of eliminating the difference between the single and double bonds of the conventional formulæ, and replacing each by a covalence and electrovalence; they also make the formulæ of the ions symmetrical as regards the three oxygen atoms, and thus bring them into line with the crystallographic data where previously it was customary to write them unsym-

metrically as * $\text{O}=\text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{O} \end{array}$ and $\text{O}=\text{N} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{O} \end{array}$.

It is of interest to note that formic acid, CH_2O_3 , maintains its stability in very much the same way as hypophosphorous acid by becoming monobasic, so that the ion is $\bar{\text{O}} - \overset{+}{\text{C}}\text{H} - \bar{\text{O}}$, and not $\bar{\text{O}} - \text{C} - \bar{\text{O}}$, where the central carbon atom would be neutral instead of carrying a stabilizing positive charge. This neutrality of the central atom can, of course, also be used

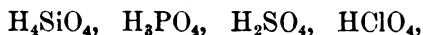
* The "symmetrical" formula for the nitrates was given by Latimer and Rodebush, but without the electric charges shown above.

to explain the instability of orthocarbonic acid, H_4CO_4 , or



which neutral atoms are held together by covalencies, are quite stable; as shown above, the central atom of the ion acquires a positive charge when orthocarbonic acid passes into carbonic acid, and the carbonates derived from the latter acid are fairly stable.

Finally, attention may be directed to the fact that the old conception of "ortho-acids" in which all the oxygen is present as hydroxyl, *e. g.* $\text{Si}(\text{OH})_4$, $\text{P}(\text{OH})_5$, $\text{S}(\text{OH})_6$, $\text{Cl}(\text{OH})_7$, has no significance whatever, since the octet theory imposes a limit of four on the primary covalency of all the lighter elements. It is therefore very doubtful whether any of these acids, except silicic acid, can exist, unless as "molecular compounds" held together by residual electrovalencies, *i. e.* by stray fields from primary electrovalencies such as have been postulated in the formula for sulphuric acid. The place of the old "ortho-acids" is taken by the series of acids and ions which contain four oxygen atoms, as in

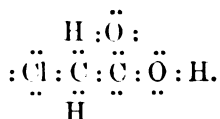


where the maximum covalency of four is reached; at the same time the maximum development of electrovalency makes these acids and ions more stable than those containing less oxygen.

4. Acidifying Properties of Oxygen.

The theory of intramolecular ionization leads to a novel explanation of those acidifying properties which led Lavoisier to bestow the name of oxygen upon this element. In general, acidity may be traced to the repulsion between a heavy positive nucleus and the light nucleus of a hydrogen atom; this results finally in the expulsion of the latter in the form of a detached proton or hydrogen ion, which leaves behind its electron in the form of a negative charge on the anion. The repulsive force increases progressively in the series $\equiv\text{CH}$, $=\text{NH}$, $-\text{OH}$, ClH , partly because of the increased weight of the nucleus, but apparently also in some inverse proportion to the number of hydrogen nuclei on which the repulsion acts.

This last effect appears to find an explanation in the observations of Rankine (Trans. Faraday Soc. xvii. p. 719, 1922) on the collision areas of the hydrides. These observations have shown that the size of the octet increases progressively from neon to methane, perhaps because of the mutual repulsion of the adherent hydrogen nuclei, but also as an obvious result of the weakened grip of the central nucleus on the surrounding electrons as protons are transferred from the inside to the outside of the shell. If these sizes are regarded as fixed, it is clear that the repulsive action of the nucleus in hydrogen fluoride as compared with that in methane may increase much more rapidly than its mass since Bohr has calculated that the electric field outside an octet would vary as the *tenth* power of the distance from the nucleus (see Langmuir, Trans. Faraday Soc. xvii. p. 609, 1922). This repulsion can apparently be transmitted through a series of atoms, since a relatively distant chlorine atom produces a marked increase of acidity in compounds such as the chloracetic acids, where the chlorine is separated from the hydrogen by a chain of two carbons and one oxygen, thus



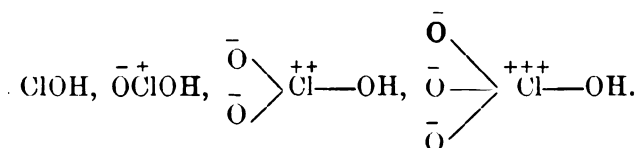
In all such cases the mechanism by which the repulsion is transmitted would appear to be a displacement of the nuclei relatively to the shells of electrons (compare Langmuir, Trans. Faraday Soc. xvii. p. 609, 1922), *e.g.* from left to right in the above formula, thus increasing the final repulsion of the nucleus of the hydroxylic oxygen for the terminal hydrogen nucleus which is split off as an ion. Whatever the mechanism may be, however, it is clear that the effect is cumulative for several halogens, but diminishes rapidly and progressively as the line of intervening atoms is lengthened.

A more effective way of increasing the repulsion is, however, to add a positive charge to the repelling atom; and this can be done by bracketing it with an oxygen atom, as described in the preceding section, since under these conditions the oxygen atom always acquires a negative charge, whilst a positive charge is transferred to the atom which is bracketed by it. The effect of this is seen on comparing the neutrality of alcohol, $\text{CH}_3\text{—CH}_2\text{—OH}$, with the weak

acidity of acetic acid, $\text{CH}_3\text{—}\overset{+}{\text{C}}\begin{array}{l} \nearrow \bar{\text{O}} \\ \searrow \text{OH} \end{array}$, where the positive

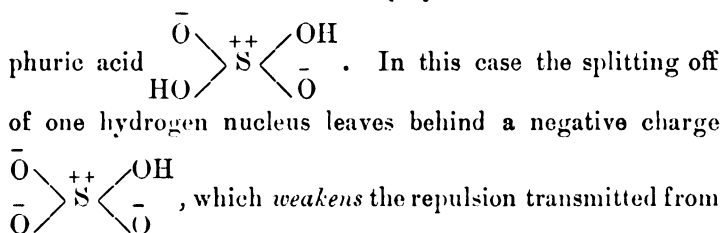
charge on the carbon atom transmits through the hydroxylic oxygen a repulsion just sufficient to enable the terminal hydrogen nucleus to escape as an ion. The direct effect of the carboxyl oxygen is probably small, since the repulsive action of its heavy nucleus is largely neutralized by the negative charge which it carries.

On the same basis the acid $\text{H}-\overset{+}{\text{Cl}}-\bar{\text{O}}$ or $\text{H}-\text{Cl}=\bar{\text{O}}$ would be stronger than hydrochloric acid; but in practice the hypothetical oxy-acid passes (as described above) into the more stable electrically-neutral molecule $\text{H}-\text{O}-\text{Cl}$, where the repulsive action of the chlorine is now required to operate through an oxygen atom, so that the compound is weaker than hydrochloric acid instead of stronger. When, however, the chlorine is now bracketed with additional oxygen atoms, each of these contributes an additional positive charge to the chlorine, and makes the acid not only more stable but also stronger in the series



This procedure is, however, limited to the introduction of four oxygen atoms, since the octet is unable to carry any larger number of nuclei.

The converse process of diminishing the acidity of a compound by imposing a negative charge on one of the repelling atoms is most familiar in the polybasic acids, such as sul-



the nucleus of newly-ionized oxygen atoms through sulphur and oxygen to the second hydrogen nucleus, and so makes HSO_4 a weaker acid than H_2SO_4 . In the same way the progressive diminution of acidity in the series HClO_4 , H_2SO_4 , H_3PO_4 , H_4SiO_4 may be associated with the diminishing positive charge on the central atom of the ion, thus $\overset{+++}{\text{Cl}}$, $\overset{++}{\text{S}}$, $\overset{+}{\text{P}}$, Si , as well as with the diminishing mass of the nucleus.

5. *Influence of Intramolecular Ionization on Physical Properties.*

It will be noticed that in Sir Joseph Thomson's classification carbon dioxide and nitrous oxide both appear in Group I. as non-ionized molecules. It therefore remains to examine how far the views set out above are in harmony with the observed physical properties of these gases, and for this purpose the exact effect of the rearrangement of the nuclear charges on passing from one gas to the other must be considered. In the first place, it should be noticed that the repulsion between the nuclei of C and O will be very similar to that between N and N, since if these forces can be assumed to be governed still by the law of inverse squares, the repulsions would be in the ratio 48 : 49. In the second place, the view has been adopted that the nuclei are not rigidly fixed in the centre of the enveloping octets, but are able to adjust themselves to the attracting and repulsive forces acting upon them. Under these conditions it may be doubted whether any important stray field of force would escape beyond the cage of electrons in which all the nuclei are embedded. This conclusion is indeed almost inevitable in view of the fact that the similarity of the gases appears, not only in their refractive indices and specific inductive capacities, but also in the much wider range of physical properties tabulated by Langmuir. On the other hand, the stability and other chemical properties of the molecule which depend on fields of force *within* the molecule may be influenced very profoundly, on the lines discussed in the present paper, by these internal electrical forces.

6. *Summary.*

(1) Internal ionization is postulated in a number of compounds where the charges on the nuclei are not balanced by the enveloping electrons.

(2) Stability in oxy-acids depends on the presence of a positive charge on the central atom of the ion. This also increases the strength of the acid.

(3) A maximum of stability and of strength is reached in acids containing four atoms of oxygen round the central atom of the ion.

University Chemical Laboratory,
Cambridge.

CXVI. *Note on the Theory of the Specific Heat of Liquids.*

By F. A. LINDEMANN*.

IN the January number of the Philosophical Magazine Professor Honda has put forward a theory of the specific heat of liquids which can scarcely be allowed to pass unchallenged. It applies primarily to monatomic substances, and may briefly be outlined as follows:—The atoms in a solid execute translational vibrations according to the usual theory with the mean energy $3R/(\theta_1/T)$, θ_1 being the characteristic temperature and $f(\theta_1/T)$ the function which according to the quantum theory determines the energy content. In addition to this, he assumes the atoms to carry out rotational oscillations about their centre of gravity in the solid, being constrained by the directive forces of the neighbouring atoms. Fusion he assumes to occur at the temperature at which the energy of these rotational vibrations becomes so large that the atoms execute continuous rotations. He neglects the work done against cohesion in the change of volume on fusion, and explains the latent heat of fusion as the energy which these new degrees of freedom of continuous rotation must acquire. Deviations from the atomic heat in the liquid proper to the three translational degrees of freedom plus two or three rotational degrees of freedom are explained by supposing that the potential energy in the translational oscillations may diminish if the atom executes long unconstrained free paths like the atoms in a gas.

Apart from the first generally accepted view of the translational vibrations, scarcely one of these assumptions is free from objection.

Atoms cannot rotate about their centres of gravity, as their moments of inertia are much too small. They are of the order Σmr^2 , where m is the mass of one electron and r its mean distance from the nucleus, and are clearly less than 10^{-42} . Since $I\nu$ must be $4\pi^2nh$, I being the moment of inertia, ν the frequency of rotation, n an integer, and h Planck's constant, therefore ν would have to be of the order 10^{17} , i. e. the characteristic temperature θ of the order $5 \cdot 10^6$. It is evident that rotation at ordinary temperatures is impossible, on account of the factor $e^{-\theta/T}$. If the atoms could execute rotational oscillations the energy of the solid would be larger than $3Rf(\theta_1/T)$ by an amount $3Rf(\theta/T)$, θ being the characteristic temperature corresponding to the rotational frequency. On melting, if Prof. Honda's theory were true, these oscillations would become complete

* Communicated by the Author.

rotations and the potential energy would become free, *i. e.* a negative heat of fusion would result. If atomic rotations really occur in fluids, they must occur in a gas. If this were so, the atomic heat of mercury vapour would be $3R$ and the ratio of the specific heats 1.333... instead of the observed value of 1.67. The work done against cohesion by expansion on fusion is by no means negligible, as is assumed, but amounts to about half the latent heat. Finally, the atoms could only execute free paths without constraint if they were comparatively far apart. On fusion, their mean distance in general increases by little more than 1 per cent. If their amplitude of oscillation is 12 per cent. on fusion, therefore at most 1/13 of their paths could be executed under diminished constraint and hence no material diminution of the potential energy can take place.

For each and all of these reasons, Prof. Honda's theory must therefore be rejected. To avoid ambiguity, it may perhaps be worth while briefly to restate the theory which I had believed to be currently accepted.

Under the influence of their mutual attractions and repulsions the atoms in a solid form a space-lattice, regular in crystals, irregular in glasses. Their thermal energy at constant volume is in the form of translational oscillations, whose frequency is determined by the mass and the restoring force. A simple application of Taylor's theorem shows that the restoring force is elastic for small displacements, but does not remain so for large displacements. Hence the mean potential energy equals the mean kinetic energy at low temperatures, but may exceed it near the melting-point. At the melting-point some discontinuities in the atom collide or overlap, presumably orbits of peripheral electrons. Hence a crystal has a sharp melting-point, a glass an indefinite one. Monatomic solids expand on fusion, and about half the latent heat is simply work done against the cohesive forces. On account of the greater distance between the atoms in the liquid, the restoring force is less than in the solid and consequently the atoms' frequency and the characteristic temperature θ_2 must be lower. The balance of the latent heat is therefore probably accounted for by a term

$$3R \int_0^{T_m} (j(\theta_1/T) - j(\theta_2/T)) dT.$$

This point of view appears to account for the facts quite adequately and consistently, and unless Prof. Honda can show that it involves difficulties comparable to those inherent in his theory it would seem preferable to adhere to it.

CXVII. *The Total Reflexion of X-Rays.* By ARTHUR H. COMPTON, Ph.D., Wayman Crow Professor of Physics, Washington University, Saint Louis*.

1. Deviations from Bragg's Law.

THOUGH direct attempts to measure the index of refraction of different substances of X-rays have hitherto failed, deviations from Bragg's relation,

$$n\lambda = 2D \sin \theta,$$

have been observed which have been ascribed to an appreciable refraction of the X-rays as they enter the crystal. These deviations were first observed by Stenström †, using wave-lengths greater than 2.5 Å.U. Duane and Patterson ‡ and Siegbahn § have also noticed that even with ordinary X-rays the wave-lengths calculated from measurements in the different orders of reflexion do not exactly agree with each other. Stenström's conclusion that these experiments indicate appreciable refraction was criticized by Knipping ¶; but a more careful analysis by Ewald ¶¶ shows a quantitative agreement between the discrepancies observed by Stenström and those calculated on the refraction hypothesis.

The fact that Bragg's law cannot be strictly true seems to have been pointed out first by Darwin **, who gives for the difference between the observed glancing angle θ and the angle θ_0 anticipated from Bragg's formula,

$$\theta - \theta_0 = \delta / \sin \theta \cos \theta.$$

Here

$$\delta = 1 - \mu,$$

where μ is the index of refraction of the X-rays in the crystal. An expression which gives the index of refraction from measurements of the glancing angle for different orders of reflexion is

$$\delta = \frac{\lambda_1 - \lambda_2}{\lambda_2} \cdot \frac{n_2^2}{n_2^2 - n_1^2} \sin^2 \theta_1, \quad \dots \quad (1)$$

where λ_1 and λ_2 are the apparent wave-lengths as measured

* Communicated by the Author.

† W. Stenström, Dissertation, Lund (1919).

‡ Duane and Patterson, *Phys. Rev.* xvi. p. 532 (1920).

§ M. Siegbahn, *Comptes Rendus*, clxxiii. p. 1350 (1921); pp. 174, 745 (1922).

¶ P. Knipping, *Zeits. f. Phys.* i. p. 40 (1920).

¶¶ P. P. Ewald, *Phys. Zeits.* xxi. p. 617 (1920).

** C. G. Darwin, *Phil. Mag.* xxvii. p. 318 (1914).

in the n_1 and n_2 orders respectively, and θ_1 is the glancing-angle for the n_1 order*. If the index of refraction of the crystal is known, the true wave-length can be calculated from the formula,

$$n\lambda = 2D \sin \theta \left(1 - \frac{\delta}{\sin^2 \theta} \right). \quad (2)$$

Duane and Patterson† find an apparent difference in the wave-length of the tungsten $L\alpha$ line, $\lambda = 1.473 \text{ \AA}$., as observed in the first and second order from calcite, of $\lambda_1 - \lambda_2 = 0.00015 \text{ \AA}$. According to equation (1), this means an index of refraction less than unity by $\delta = 8 \times 10^{-6}$. Their similar measurements on 1.279 and $1.096 \text{ \AA}$. give $\delta = 10$ and 3×10^{-6} respectively.

2. Drude-Lorentz Theory of Dispersion.

According to the Drude-Lorentz theory of dispersion‡, the index of refraction of a medium for radiation of very high frequency is given approximately by

$$\delta = 1 - \mu = \sum \frac{n_r e^2}{2\pi m(\nu^2 - \nu_r^2)}. \quad (3)$$

Here n_r represents the number of electrons per unit volume which vibrate with the natural frequency ν_r , e and m have their usual significance, ν is the frequency of the radiation, and the summation is taken over the different types r of the electrons. If, as in the case of ordinary X-rays traversing matter composed of light atoms, the frequency of the

* Darwin's investigation shows that, in spite of the fact that the wave-length is less than the distance between the individual atoms, refraction problems may be treated in the usual manner. If then θ and λ are the glancing angle and wave-length respectively outside the crystal, and θ' and λ' the corresponding angle and wave-length within the crystal,

$$\frac{\lambda}{\lambda'} = \mu; \text{ and } \frac{\cos \theta}{\cos \theta'} = \mu, \text{ or } \frac{\sin \theta'}{\sin \theta} = \frac{1}{\mu} \left(1 - \frac{1 - \mu}{\sin^2 \theta} \right).$$

But Bragg has shown that

$$n\lambda' = 2D \sin \theta';$$

whence

$$n\lambda = 2D \sin \theta \left(\frac{1 - \mu}{\sin^2 \theta} \right),$$

which is equation (2). This gives the true wave-length in terms of the known grating space and the observed glancing angle. To determine the index of refraction, the glancing angles θ_1 and θ_2 for two different orders n_1 and n_2 must be measured. This gives two equations (2), from which the unknown wave-length λ may be eliminated, giving, after some reduction, equation (1).

† Duane and Patterson, *loc. cit.*

‡ Cf., e.g., H. A. Lorentz, 'The Theory of Electrons,' 2nd ed. p. 149.

radiation is considerably higher than the natural frequency of the electrons, this becomes very nearly,

$$\delta = \frac{ne^2}{2\pi m\nu^2}, \quad \dots \dots \dots (4)$$

where n is the total number of electrons per unit volume of the medium.

If X-rays of wave-length $1.473 \text{ \AA}$. traverse calcite, this expression (4) indicates an index of refraction which is less than unity by about 8×10^{-6} . For $\lambda = 1.279$, $\delta = 6 \times 10^{-6}$, and for $\lambda = 1.096$, $\delta = 4.5 \times 10^{-6}$. The close correspondence between these theoretical values and the values calculated from Duane and Patterson's experiments can leave little doubt but that the consistent changes in apparent wave-length with order which they observe are due to refraction.

3. Observation of Total Reflexion of X-rays.

Since the refractive index is less than unity, a beam of X-rays striking a plane surface at a sufficiently large angle of incidence should be totally reflected. The critical glancing angle is given by

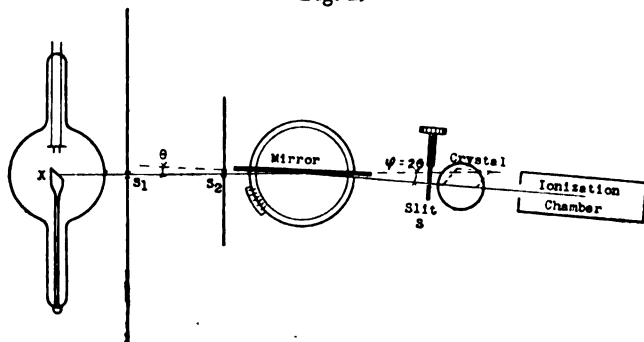
$$\cos \theta = \mu,$$

or

$$\sin \theta = \sqrt{2\delta}.$$

For $1.279 \text{ \AA}$., the value of δ for crown glass of density 2.52 is given by equation (4) as 5.2×10^{-6} , in which case $2\theta = 22$ minutes of arc, which is a readily measurable deflexion*.

Fig. 1.



In searching for the totally reflected beam, the apparatus was set up as shown diagrammatically in fig. 1. The beam of X-rays passing through the slits S_1 and S_2 had an effective

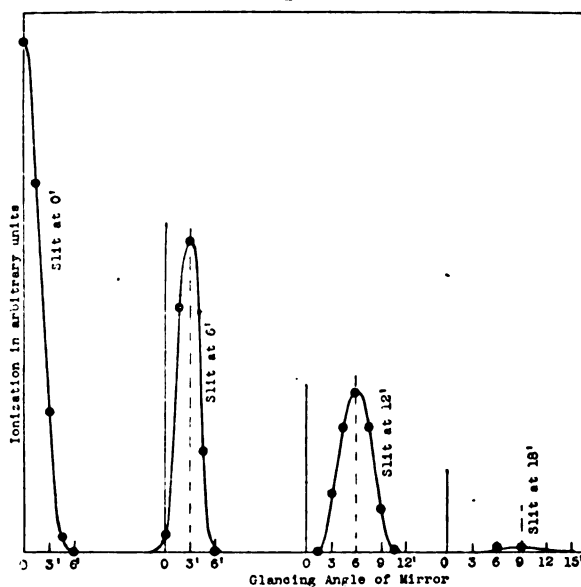
* In this calculation, the composition of crown glass was assumed to be $\text{CaO} \cdot \text{Na}_2\text{O} \cdot 2\text{SiO}_2$. However, for a given density, variations in the composition affect only very slightly the index of refraction as calculated from equation (4).

width of about 2 minutes of arc. The mirror was a piece of ordinary plate glass, of density 2.52, mounted upon the prism table of a spectrometer. The vernier of the spectrometer was used only to check the accuracy of a lamp and scale system, which was set at such a distance from the mirror that a rotation of the mirror through an angle of $\theta = 1$ minute gave a deflexion of 1 mm. The slit S could be moved by a micrometer screw through any desired angle ϕ , while the opening into the ionization chamber was wide enough to admit rays coming from the mirror through a range of about 1.5 degrees.

The zero position of the slit S was determined by removing the mirror and adjusting the slit S for maximum deflexion. The zero position of the mirror could not be determined by the maximum deflexion, since, as we shall see, the beam reflected from the surface is nearly as intense as the primary, so that the maximum deflexion is not given when the front surface of the mirror just bisects the primary ray, but when part of the primary ray is reflected from its front surface. A more satisfactory method of determining the mirror's zero point was to turn it until the visual image of the slit S_1 coincided with the real slit.

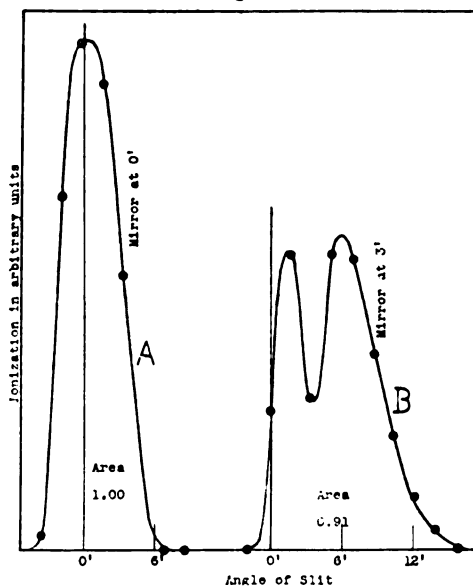
In searching for the predicted total reflexion, the slit S was moved several minutes of arc from the zero position, and the ionization current noted for various positions of the mirror. The results thus obtained, for different positions of the movable slit, are shown in fig. 2. For example, when the slit was at an angle $\phi = 12'$, on turning the mirror from zero to $12'$ the intensity of the X-rays entering the chamber increased from zero at small angles to a maximum at $6'$ and then fell to zero at larger angles. If the X-rays entering the chamber were diffusely scattered, they should have been of maximum intensity when the mirror was at the smallest glancing angle at which all the primary beam would impinge upon its front surface, *i. e.* at about $4'$. Thus the fact that the X-rays are in every case of maximum intensity when the angle $\phi = 2\theta$ shows that there is an approximately specular reflexion of the X-rays at these small angles. The increasing breadth of the reflected beam at the larger angles shows that the reflexion is not perfectly regular. It appears rather that the glass surface reflects the X-rays in much the same manner that the air above a heated street reflects light to form a mirage. The fact that no appreciable reflexion is observed at angles as great as $\phi = 18'$ means that for the greater part of the X-ray beam the critical glancing angle θ is less than $9'$.

Fig. 2.



The maximum intensity occurring when the glancing angle of the mirror is half that of the slit indicates specular reflexion.

Fig. 3.



The reflected energy is nearly equal to the incident energy, indicating total reflexion.

If the observed phenomenon is really one of total reflexion, the energy in the reflected beam should be nearly as great as that in the primary beam. A measure of the total energy in each beam was obtained by integrating the observed ionization as the slit S was moved across the beam. Curve A of fig. 3 was thus obtained when the mirror was set at zero, and curve B when at $3'$. This small glancing angle was necessary in order not to exceed the critical angle for the shorter wave-lengths. In order to satisfy this condition with greater certainty, the tube was operated at the comparatively low potential of about 12,000 peak volts. But the angle was so small that part of the primary beam was not intercepted by the mirror, giving rise to a sharp peak at $1'5$ in curve B. The ratio of the areas of the two curves, 0.91, shows that the greater part of the incident energy is indeed reflected.

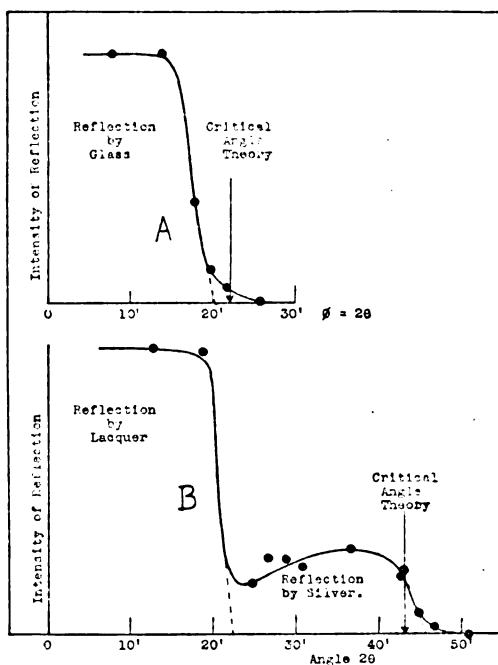
4. *The Index of Refraction for X-rays.*

In order to test quantitatively the theoretical dispersion formula for these very high frequencies, it was necessary to determine the critical glancing angle for a known wave-length. For this purpose the calcite crystal C, on the crystal table of a Bragg spectrometer, was placed in the path of the reflected beam, so that its spectrum could be studied. The procedure then consisted in measuring the intensity of a given spectrum line in the beam reflected from the mirror, and in finding the angle $\phi = 2\theta$ beyond which the line fails to appear. The results of these experiments are shown in fig. 4. Curve A shows the intensity of the reflexion of the tungsten L line $\lambda = 1.279 \text{ \AA.}$ by the plate-glass mirror at various angles $\phi = 2\theta$. It will be seen that the line has almost disappeared from the reflected beam at a critical glancing angle of about $20'$. Curve B shows the intensity of the same line as reflected from the surface of a silvered glass mirror coated with a thin film of lacquer. It is apparent that the critical angle for the lacquer is passed at about $22'$, while the line finally disappears not far from the angle $43'$ predicted by Lorentz's theory as the critical glancing angle for silver. From these curves we may take the critical glancing angle for glass as $\theta = \phi/2 =$ about $10'$, for lacquer as about $11'$, and for silver as about $22'5$. These values correspond to indices of refraction less than unity by 4.2×10^{-6} in the case of glass, 5.1×10^{-6} in the case of lacquer, and 21.5×10^{-6} in the case of silver.

The spectrum of the rays reflected from glass at the angle

$\phi=8'$ is shown in fig. 5, curve A, as compared with the spectrum of the primary beam, curve B. The ordinates of the spectrum of the reflected rays are magnified by a factor of 3. It will be noticed that whereas the spectrum of the primary rays begins at $\theta=2^{\circ}1'$, corresponding to a wave-length of $0.22 \text{ \AA.}$, the spectrum of the reflected rays begins rather gradually at about $4^{\circ}5'$, and apparently, if the slits

Fig. 4.

Total reflexion and critical angles for $\lambda=1.279 \text{ \AA.}$

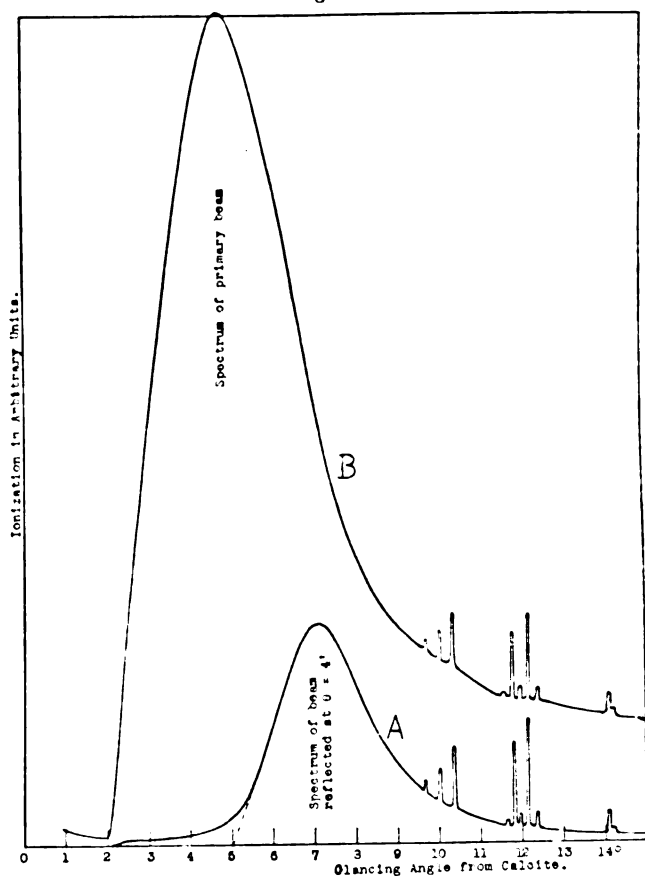
were sufficiently narrow, would begin at about $5^{\circ}0'$. Thus $\phi/2=4'$ is the critical angle for a wave-length of about $.52 \text{ \AA.}$, corresponding to a value of $1-\mu=0.9 \times 10^{-6}$. This value is not, however, as reliable as the values obtained from the spectrum line.

5. Comparison of the Experiments with Theory.

The calculation of the index of refraction of crown glass is not difficult, since the frequency of the radiation employed is considerably higher than that of the K absorption

band of the heaviest element, calcium, in the glass. Consequently, the simple formula (4) can be applied with very little error. In the case of silver, however, the wave-length employed, $1.279 \text{ \AA.}$, is intermediate between the critical K and L absorption frequencies. It is thus necessary to take into account the natural frequencies of the electrons in both

Fig. 5.



of the inner rings. It is surprising, however, how small a difference the corresponding degree of resonance makes. Thus if the middle of the K absorption band is taken as $3.9 \text{ \AA.}$, that of the L series as $2.9 \text{ \AA.}$, the number of electrons in the K ring as 2, and in the L ring as 8, the value of δ , according to equation (3), is 19.8×10^{-6} ; but the approximate equation (2) gives the corresponding value as 20.3×10^{-6} , a difference of only 2 per cent.

In Table I. are given the results of the experimental measurements of the index of refraction as compared with the theoretical values for glass, silver, and lacquer.

TABLE I.

Substance.	Density.	Wave-length Å. U.	Critical angle θ , expt.	$\delta = 1 - \mu$, experiment.	$\delta = 1 - \mu$, theory.
Glass.....	2.52	1.279	10'	4.2×10^{-6}	5.2×10^{-6}
Glass.....	2.52	.52	4'	0.9×10^{-6}	0.7×10^{-6}
Silver ...	10.5	1.279	22'.5	21.5×10^{-6}	19.8×10^{-6}
Lacquer..	—	1.279	11'.0	5.1×10^{-6}	—

It is at first sight surprising that the value of δ should be greater for lacquer than for glass. Some recent experiments by Miss Laird have indicated*, however, that the density of thin films of celluloid increases considerably as the films become very thin, rising from the value of 1.41 for thick films to greater than 2.5 for the thinnest films measured. In view of the hydrogen content of these organic substances, it thus appears that the electron density in these dense thin films is greater than in glass. Thus in every case the experimental values of the index of refraction are in satisfactory accord with the usual electron theory of dispersion†.

6. Application to Physical Problems.

This establishment of the theoretical dispersion formula makes it possible to calculate with accuracy the index of refraction for these very high frequencies by substances containing only the lighter atoms. There remains some uncertainty with regard to the natural frequencies of the K and L electrons in the heavier elements; but as we have seen in the case of silver, errors from this cause can hardly be serious. Fortunately, the crystals most used in X-ray spectroscopy are composed of relatively light elements. In the case of calcite, formula (4) gives the value of $1 - \mu$ as $3.67\lambda^2 \times 10^{-6}$, where λ is expressed in Ångström units. As compared with formula (3), this expression is accurate to 1 per cent. for wave-lengths less than 2 Å., and is accordingly reliable for corrections of the wave-length throughout the usual X-ray spectrum. The corresponding expression for

* E. R. Laird, Phys. Rev. xix. p. 384 (1922).

† There is an apparent tendency for the experimental value of $1 - \mu$ for glass to fall below its theoretical value, though the difference is hardly more than the experimental error. If the difference is real, it may indicate the existence of a thin layer of matter of low density, such as water or oxygen, on the surface of the glass.

rock-salt is $3.04\lambda^2 \times 10^{-6}$, which should also be accurate to 1 per cent. over the same range. Using these values for the index of refraction, the true wave-length can be calculated from the glancing angle according to equation (2).

A matter of considerable interest is the prominence of the L series spectrum lines in the spectrum of the totally reflected rays. In the primary beam, operating the tube at about 70,000 peak volts and using a wide opening into the ionization chamber, the continuous background is more prominent than even the strongest of the L series lines. But when wave-lengths shorter than 0.5 Å. are absent, as they are in the reflected beam, the spectrum lines stand out much more prominently. In fact, the continuous background has almost disappeared. It is obvious from this result that the principal part of the continuous background in this region consists of the higher orders of reflexion of the shorter wave-lengths, and that comparatively little energy of wave-lengths greater than 1 Å. occurs in the general radiation.

This experiment illustrates the use of the phenomenon of total reflexion as a means of filtering the *short* wave-lengths from a beam of X-rays, a result which cannot be secured by absorption filters. Unfortunately the method can be applied only in the case of very narrow beams of X-rays, having a breadth of the order of a few minutes of arc. But in the case of such beams, the reflexion is so nearly total that the reduction in intensity is not great, while the critical glancing angle is so well defined that the shorter wave-lengths are rather sharply cut off. For use as such a filter, a mirror with a platinum surface is to be recommended, because its index of refraction differs so greatly from unity that the critical angles are comparatively large.

The existence of an index of refraction of the magnitude predicted by the classical electron theory would seem irreconcilable with the view that one quantum of X-rays can affect but a single electron. For there would seem to be no possibility of refraction unless the ray can spend a part of its energy in setting in vibration some of the electrons over which it passes so as to give rise to a secondary ray which will combine with the primary train. But this involves the idea that parts of the quantum are capable of affecting the traversed electrons. It is not easy to reconcile this result with such experiments as that of the softening of scattered X-rays*, which seem to demand that each electron affected by the primary rays receives both the momentum and the energy of a whole quantum.

* Cf. A. H. Compton, Bulletin Nat. Research Council, No. 20, p. 16 (1922).

It is of value to note that equation (4) supplies a means of determining with fair accuracy the wave-length of an X-ray beam from an experimental measurement of its index of refraction, if the number of electrons per unit volume is known. If the number of effective electrons per atom is taken equal to the atomic number, as X-ray scattering experiments show is at least approximately the case, the measured value $\lambda = 4.2 \times 10^{-6}$ for glass means a wave-length of 1.18 Å. This value is independent of any knowledge of crystalline structure or of the energy quantum, and so gives a very valuable confirmation of the wave-length 1.28 Å. calculated on the basis of other more accurate though less fundamental methods.

Perhaps of greater importance is the fact that, knowing the wave-length, it is possible to calculate from the observed index of refraction the number of electrons per atom which are affected by the incident X-rays. In calculating the theoretical value of the index of refraction from formula (3), the number of electrons per atom has been taken equal to the atomic number. From the accuracy with which the index as thus calculated agrees with the experiments, it follows that this assumption is probably correct to within about 5 per cent.

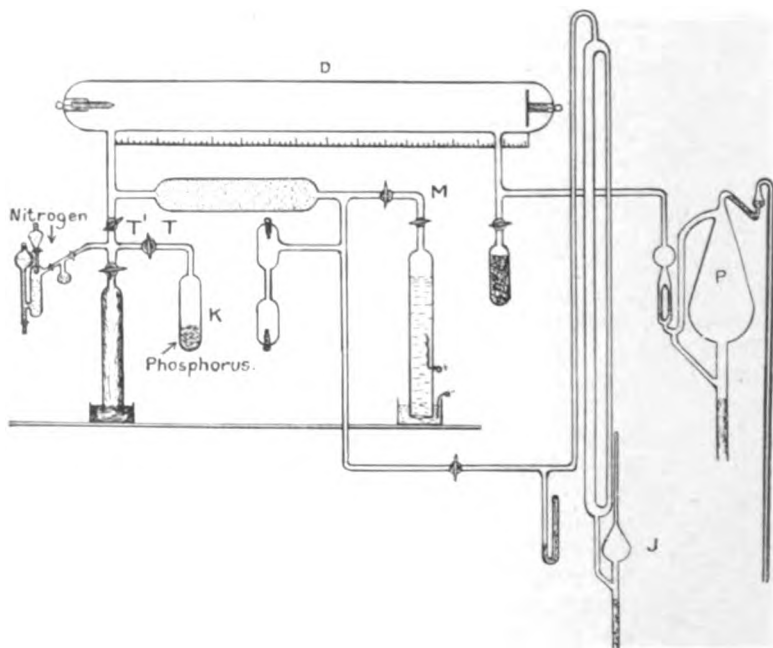
The two most direct methods hitherto employed for determining the number of electrons in the outer part of the atom are the study of the scattering of alpha rays by atomic nuclei and the measurement of the intensity of scattered X-rays. The first method determines the charge on the atomic nucleus, and it is not certain *à priori* that the charge thus measured is identical with the charge on the electrons which are responsible for high frequency radiation. The intensity of the scattered X-rays, on the other hand, though determined by the electrons exterior to the nucleus, is a function not only of their number but also of their arrangement and size. The index of refraction is theoretically independent of the arrangement and size of the electrons, and depends upon their resonance only to the same extent as does the scattering. Thus an estimate of the number of mobile electrons in an atom based upon a measurement of the index of refraction is more reliable than a similar estimate based upon these other methods. It is accordingly gratifying that such a measurement confirms the result of the earlier work, indicating that the number of electrons per atom which are affected by high frequency radiations is equal to the atomic number.

Washington University,
St. Louis,
Dec. 6, 1922.

CXVIII. *Luminous Pulsations in the Glow of Phosphorus.*
*By H. P. WARAN, M.A., Ph.D. (Cantab.), F.Inst.P.**

LORD RAYLEIGH has recently called attention† to the remarkable travelling pulses of luminosity observed when oxygen comes into contact with phosphorus vapour. Following the earlier procedure of Joubert he has examined the travelling pulses of luminosity, using the method of allowing atmospheric air (containing oxygen) to leak slowly into a space in which phosphorus vapour is being continually produced by a lump of phosphorus. About two years ago I happened to observe the phenomenon of the periodic luminosity of phosphorus in somewhat different circumstances, with an apparatus of the form shown in fig. 1, which was

Fig. 1.



being used for quite a different purpose. Since my observations differ in some respects from those of Lord Rayleigh in the paper referred to, it may be of some interest if I set out the facts of my observation in some detail.

* Communicated by Prof. A. W. Porter, D.Sc., F.R.S., F.Inst.P.

† Proc. Roy. Soc. A, xc. p. 372 (1921).

In the apparatus of fig. 1, K is the side tube containing a little phosphorus used to free the apparatus from traces of oxygen; while M is the arrangement by which a small bubble of electrolytic oxygen could be introduced into the system whenever required. D is a large discharge-tube over 50 centimetres in length and about 4 centimetres in diameter, and connected to it are the Töpler pump P and McLeod gauge J. The taps T and T' having been kept open for some time, the whole of the apparatus became fouled by the phosphorus vapour and the thin deposit of phosphorus all over the glass surface could be readily seen by the change in tint throughout. Experimenting under conditions of total darkness in the room, when a bubble of oxygen was let into the apparatus the short flash of luminosity throughout the apparatus was followed by bright and practically momentary flashes of luminosity in the wider portions of the pump P and the McLeod gauge J. The perfectly dark and comparatively long intervals between the flashes of luminosity were of the order of about twenty seconds to start with. This period diminished gradually until, after about twenty to thirty flashes, the luminosity was faint and the pulsations, if any, too difficult to be followed with certainty.

It was interesting to note that the smaller bulb of the McLeod gauge showed a shorter period and a lesser number of flashes and these flashes were quite out of phase with those occurring in the bigger bulb of the mercury pump. No flashes except the initial one on the first entry of oxygen were noticed in the large discharge-tube D.

The bulbs of the pump and gauge are connected to the rest of the apparatus by comparatively long and narrow tubing. Through these there was the possibility of a kind of damped oscillation of the gas between these bulbs and the large volume of the discharge-tube, maintained by the periodic explosions occurring at these bulbs at the far end. But difficulties were encountered in pursuing this line of explanation further. Though the circumstances of the travelling pulses of luminosity discussed by Lord Rayleigh and those of the periodic luminosity observed by the author are different, it is possible that the explanation for both is based on the same primary cause.

Though I had set aside this interesting observation for investigation at a more convenient opportunity, recently, since the publication of Lord Rayleigh's paper, I have tried to experiment further on the phenomenon with a view to explain some of the differences in our observations. The first difference noted by me was that whereas Lord Rayleigh

asserts the need for the presence of water vapour to maintain the travelling pulses of luminosity, oxygen dried over phosphorus pentoxide at a low pressure seems to be quite effective for producing the periodic flashes. Secondly, in my arrangement the whole of the oxygen is let in into the highly exhausted volume of the apparatus and is not gradually supplied by a process of leakage through a fine capillary tube. In these two respects amongst others the phenomenon of the periodic flashes seems to differ from the case of the travelling pulses of luminosity. It is also difficult to follow up the explanation of a travelling pulse from the circumference to the centre or *vice versa*, since on this view it is difficult to explain the further flashes after the first one has consumed all the available oxygen. It may be that by a process of damped oscillation between parts of the apparatus, or by a very slow flow of gas through the long and narrow connecting tubes, fresh supply of gas is continually available for the maintenance of the successive flashes.

To test these two possibilities further, two forms of apparatus as shown in figs. 2 and 3 were made. In fig. 2, pure dry electrolytic oxygen is stored at a low pressure in the bulb *b* over a layer of phosphorus pentoxide. The phosphorus is contained in a tube *t* immediately below the flash bulb B, and a stop-cock S separates these two volumes. Oxygen from *b* can be let into B by turning the half-filled stop-cock T, and the bubble of gas thus let in has to traverse the spiral of glass tubing before it enters the flash bulb. Because of this arrangement there is no large idle volume connected to the bulb B to permit of the oscillations of gas between the flash bulb and itself. This part of the apparatus is completely exhausted, and by opening the stop-cock S and warming the tube *t* phosphorus can be distilled over into B, where it deposits itself as a thin layer over the glass walls. This form of apparatus has the great convenience that it is complete in itself for the flash experiment. The admission of pure oxygen makes the products of combustion in the flash bulb practically disappear, leaving the vacuum in B as perfect as before, thus permitting the apparatus to be used again for observing another set of flashes. Experimenting with this apparatus, for every bubble of oxygen admitted into the apparatus a regular series of flashes was observed as expected, even after the oxygen had been dried by standing in contact with phosphorus pentoxide for over one and a half years. This proved two points. Firstly that the presence of water vapour is not essential for the maintenance of these series of periodic flashes, though it may be

necessary for the travelling pulses of luminosity. Secondly, that the flashes are not being maintained by a periodic supply of gas arising from the oscillations of gas between parts of the apparatus, with narrow connexions between them. This latter point is further supported by the observations with the similar apparatus of fig. 3, where the long spiral connecting tube is also dispensed with. To keep the large volume of the flash bulb quite dry and free from any

Fig. 2.

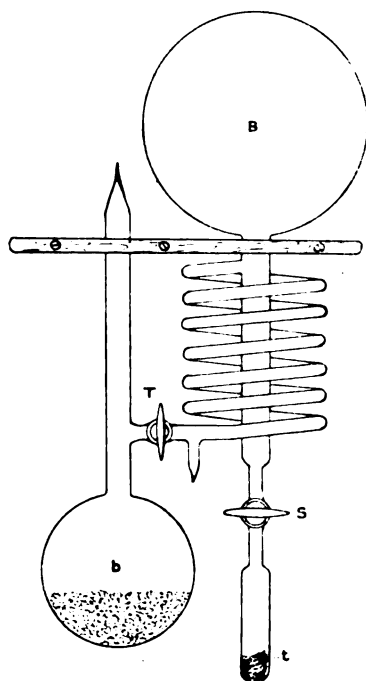
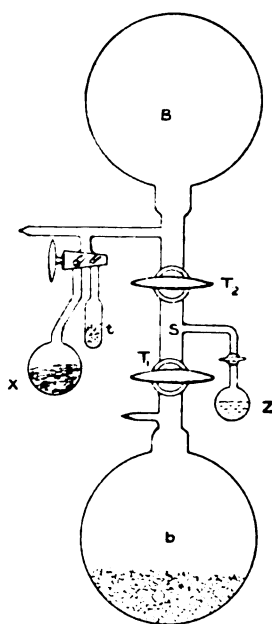


Fig. 3.



moisture introduced with the phosphorus distilled into it, a small bulb X of phosphorus pentoxide is permanently sealed on to it. A side tube leading to a bulb Z containing a little water enables water vapour to be added on to the bubble of oxygen let into the space S by turning the half-filled tap T_1 before the mixture of the two is let into the flash bulb by opening T_2 . From the experiments with this apparatus it would appear that the influence of water vapour is not anything serious, and the effect, if any, is a slightly increased luminosity in the flashes.

Experimenting with this apparatus the sequence of

changes noted as characteristic of these flashes were as follows:—

- (1) An initial luminosity for a brief interval on the admission of the bubble of gas into the system.
- (2) Its quick decay to complete darkness.
- (3) The origin of the periodic flashes.
- (4) Their continued occurrence with gradually decreasing period.
- (5) The disappearance of the final faint glow.

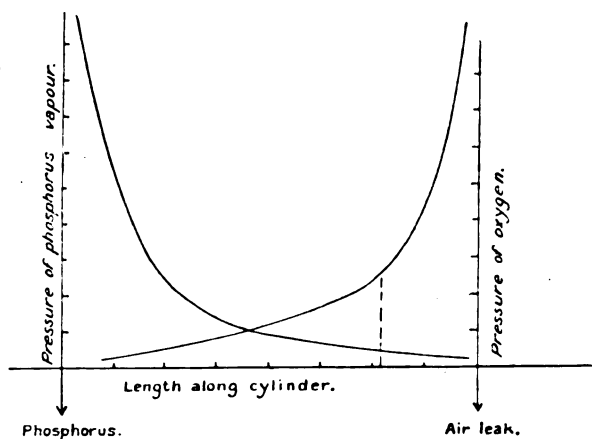
Any proper explanation of this phenomenon must be capable of satisfactorily accounting for this sequence of changes. Though the nuclear theory of Lord Rayleigh is satisfactory enough in explaining the propagation of the travelling pulses of luminosity studied by him, it does not seem to be applicable to the present case. The earlier conclusion of Joubert that below certain pressures too small to measure phosphorus would not combine with oxygen, seems to be suggestive of a profitable line of attack if we make the further assumption that the explosive or luminous combination of phosphorus vapour and oxygen is governed by the fact that, as in any explosive mixture, their partial pressure in the mixed atmosphere must bear a certain minimum ratio before combustion can spontaneously originate or be maintained in the mixture.

The validity of this assumption is proved by Lord Rayleigh's experiments on the travelling pulses of luminosity, where the luminous combination starts always at a particular level when oxygen slowly leaks into a system where a gradient in the vapour pressure of the phosphorus located at the other end exists. The situation is represented more clearly by the graphs of fig. 4, where the partial pressures of the constituents are plotted against the length of the cylinder. The change with time corresponds roughly to a vertical displacement of the partial pressure curves at different rates, and the propagation of a pulse of luminosity may be guided purely by the progressive change in this ratio at different levels along the tube. This is dependent on the rates at which oxygen and the vapour of phosphorus are flowing into each other from either end.

This line of explanation seems to suit the periodic flashes as well. For the conditions represented by the graphs of fig. 4 are exactly reproduced in the flash bulbs of the apparatus shown in figs. 2 and 3. To begin with, the inner surface of the flash bulb has a thin coating of phosphorus which is giving off inwards a slow stream of phosphorus

vapour, and there is a gradient of this pressure from the wall towards the centre when the flashes originate. The vapour of phosphorus, saturating the bulb to begin with, gets consumed by the first rush of oxygen, and this explains the initial glow. The bulb is now mainly filled with oxygen and particles of the oxide of phosphorus. The steady diffusion of phosphorus vapour into this central region of oxygen sets up in the course of a few seconds a circumferential zone of narrow width where the pressure of the phosphorus vapour is steadily increasing. As soon as it reaches the critical ratio combination results in this layer, which is seen as the first flash. This creates a situation quite favourable for the maintenance of the successive

Fig. 4.



flashes. The first flash leaves an inactive spherical zone of narrow width filled with particles of the oxides of phosphorus, and oxygen and phosphorus vapour diffuse into it from either side of it. A second flash follows when the critical ratio is reached again, and this action goes on producing the successive flashes, until the whole of the oxygen is used up. Since the pressure of oxygen falls with every flash, because of its expansion, the quantity of phosphorus vapour required to give the critical ratio decreases, and for a steady rate of evaporation of phosphorus from the walls the required vapour is formed in a shorter time and that accounts partially for the progressive diminution in the period of the successive flashes. The period suffers also a diminution because of the uncombined phosphorus vapour remaining in the region beyond the zone of active or luminous combination.

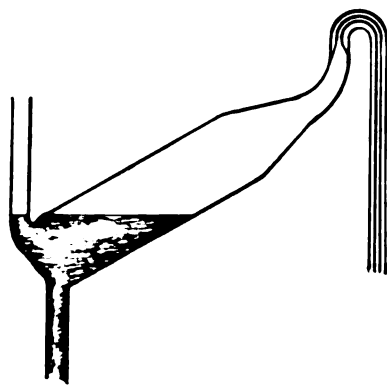
The correctness of this line of explanation can be checked by the following consequences of the explanation:—

(1) For a uniform intensity of illumination throughout this spherical layer of combination, when the bulb is viewed from the side it should show a greater intensity towards the circumference.

(2) The flashes of luminosity should not occur in the initial stages of the apparatus when there is only a little phosphorus vapour in the bulb and a layer of phosphorus has not been deposited on the walls. These are observed to be the case in practice.

Apart from these high frequency flashes with periods less than about 10 to 20 seconds there is an interesting type of long period flashes, often noticed with apparatus of large volume exhausted down to a very low pressure. A typical case of this is provided by the Töpler pump of the shape shown

Fig. 5.



in fig. 5, used to exhaust these flash apparatus. Its walls get contaminated with the phosphorus in course of time. If the apparatus connected to it contains a residual trace of low pressure oxygen and the Töpler pump be given a stroke and its cylindrical bulb watched with patience in total darkness, faint flashes with a period of the order of ten to fifteen minutes are often noticed. These flashes do not appear as instantaneous, but seem to be taking place during a definite interval of the order of a second or two during which a gradual growth and then a decay of the luminosity can be distinctly noticed. Their period also remains practically constant.

These long period flashes seem to be maintained by the slow feed of gas through the long and narrow connecting

tubes, at these very low pressures. To begin with, after the stroke of the pump, as the mercury level goes down in the pump forming the Torricellian vacuum above it, the space above gets saturated with the vapour of phosphorus evaporating from the walls. On the mercury level descending past the side tube the low pressure oxygen begins to flow in, and it takes some time before the critical ratio for the firing mixture is established, and hence the long period flash. This flash consumes the whole of the available supply of oxygen and necessitates a fresh supply flowing in for the second flash. If we raise the level of mercury at this stage and prevent the oxygen flowing into the bulb, the expected flash does not take place. This proves that it is the slow feed of gas that is responsible for the maintenance of the flashes in this case. Further, if by a few more strokes we reduce the pressure of oxygen, it ought to increase the period of the flash. This is found to be the case in practice, affording additional evidence in support of this explanation.

In conclusion, I must express my indebtedness to Prof. A. W. Porter, D.Sc., F.R.S., for his sympathetic interest in this work done at his laboratory.

University College, London.

CXIX. The Mechanism of the Electric Arc. By W. G. DUFFIELD, D.Sc., Professor of Physics in University College, Reading.*

I HAVE been greatly interested in the recent discussions in the pages of the Philosophical Magazine of the theory which I ventured to put forward in 1919 to explain the repulsion experienced by the poles of the electric arc. I hope that at this stage a few remarks from myself may not be considered out of place †.

* Communicated by the Author.

† References:—

- (1) Duffield, B. A. Report, Australia, 1914.
- (2) Sellerio, *Nuovo Cimento*, xi. p. 67 (1916). The present writer regrets that he has not seen this paper.
- (3) Duffield, Burnham, and Davis, *Phil. Trans. Roy. Soc. A.* 220. p. 109 (1919).
- (4) Duffield, Burnham, and Davis, *Proc. Roy. Soc. A.* 97. p. 326 (1920).
- (5) Ratner, *Phil. Mag.* xl. p. 511 (1920).
- (6) Tyndall, *Phil. Mag.* xl. p. 780 (1920).
- (7) Beer and Tyndall, *Phil. Mag.* xlii. p. 756 (1921).
- (8) Tyndall, *Phil. Mag.* xlii. p. 972 (1921).
- (9) Sellerio, *Phil. Mag.* xlv. p. 765 (1922).

I should like in the first instance to express my appreciation of the courteous way in which Professor Sellerio⁽⁹⁾ has drawn my attention to his own work on this subject²⁾, published in 1916. I have little doubt that the cause which led me to ignore his 1916 paper was the same as that which led him to overlook the fact that in 1914 I had presented a communication⁽¹⁾ to the British Association, entitled "The Pressure upon the Poles of a Carbon Arc" (B. A. Report, Australia, 1914). I willingly forgive him the omission of any reference to a paper published in title only, but which I think it useful to mention, as it may serve to date the first observation of this phenomenon. I am the less uneasy regarding my own oversight, because in his 1916 paper Prof. Sellerio neglected to take into account, as he very frankly admits in his 1922 paper, the forces occasioned by the magnetic field of the earth and the rest of the circuit, the elimination of which were essential before the existence of any repulsive effect could be established.

I wish also to express to Prof. Sellerio my thanks for his appreciative comments upon the accuracy of the experimental work of my fellow-workers and myself upon this effect; but at the same time I wish that he had not been content to accept our figures for the corrections for the electromagnetic effect of the rest of the circuit, and to apply them to his own observations. I can scarcely believe that the dispositions of our two sets of apparatus were sufficiently alike to justify this. I had hoped that completely independent work might settle beyond dispute whether the variation of the force with the current is truly linear or not. I confess also that I find it difficult to accept the great difference between the anode and cathode pressures calculated by Prof. Sellerio, varying from a 12 to 1 ratio to a 2 to 1 ratio. We should expect action and reaction upon the two poles to be more nearly equal, because the only way in which momentum disappears from the arc-gap is through the agency of convection currents, and these we do not find to constitute a large proportion of the whole effect. According to the experiments of Burnham, Davis, and myself, the reactions upon anode and cathode are more nearly equal—indeed, in the case most carefully considered (the 6 mm. 10 amp. arc), the mean reactions only differ by 4 per cent., an agreement which is probably accidental. We do not find any evidence of "knees" in the curves connecting current and reaction, described by Prof. Sellerio⁽⁹⁾; our graphs were all smooth, though we repeated our observations with several different dispositions of the apparatus.

The Origin of the Forces upon the Poles.

In this connexion my remarks will be confined to three headings :—

(1) *The motion of ions under the electric forces in the arc.*

In a previous paper I put forward the view that the pressure upon the poles of an arc is not to be explained by the motion of ions arising solely from the electric field within it, or, to put it more generally, that the action of the electric field upon either pole of an arc balances the reaction upon it due to its bombardment by ions whose motion the electric forces occasion. We can, for example, easily show (*loc. cit.*⁽⁴⁾) that for an ion starting from rest with charge e in a uniform field of strength R , the rate of change in the momentum delivered to the pole of opposite sign is equal to Re , which is also the electric pull upon that pole.

This rule I believe to be one of the salient features of the arc, possibly a more remarkable feature than the existence of a small pressure upon the poles; the precision with which it is obeyed may not be obvious, but it becomes apparent if we calculate upon any reasonable hypothesis the rate at which ions falling into a pole of opposite sign deliver momentum to it. If, for example, we suppose that positively-charged oxygen atoms, each carrying a charge $2e$, fall into the cathode in sufficient numbers to carry a current of 10/2 amperes in a 10 ampere arc, then, since they possess velocities induced by the potential drop just outside the pole, 11.6 volts (Duddell), that pole should experience, if there were no compensating action, a force which can easily be calculated to be of the order of seven hundred dynes. But experiment shows that the force only amounts to about 2 dynes; consequently, on the most unfavourable view, the compensation must be nearly complete, and the rule is obeyed with an accuracy of 0.3 per cent.

But the question has arisen whether the two dynes pressure results from an imperfection in the compensating mechanism, or from the impact of particles whose motion arises from some cause other than the electrostatic forces. I favour the latter, and have suggested that the outstanding pressure results from the *projection* of high-speed electrons from the cathode, whose momentum is transmitted through the body of the arc to the anode. Professor Tyndall⁽⁸⁾ has discussed the balance theory from a point of view different from that which I originally put forward, and has come to the conclusion that it should hold good for an arc between poles large compared with the arc-gap and in which the ions move

viscously, but believes that in an actual arc the lack of symmetry occasions a departure from a true balance and can account for the observed reaction.

According to him the dissymmetry may be of two types—a dissymmetry in the shape of the electrodes, such as may arise from the cathode becoming pointed, or a dissymmetry due to the acceleration of the ions under the electric field. On these grounds he disputes my theory. I do not think his objections to complete compensation well-founded; though I am not sure that I am in a position definitely to disprove his contention, the following considerations appear to me to carry weight:—

(a) If in an arc with pointed electrodes any particles carrying charges fail to strike one of the poles, the latter is deprived of the momentum which their impacts would have occasioned; the pressure upon the pole is either reduced or unaffected according to whether the charges have, or have not contributed to the attraction acting upon that pole. I do not think the pressure could be *increased* by their removal.

Moreover, Professor Tyndall's reservation concerning the pointed cathode seems unnecessary, because he deduces from an experiment with an arc with a pointed electrode, which he enclosed in a quartz tube in order to eliminate convection currents, that the lateral loss of momentum is negligible.

(b) As evidence of a lack of balance with a pointed electrode, the case of the electric windmill has been cited. But the two types of discharge have very little in common. The apparent repulsion of a pointed conductor at a high potential is due to the pull of the Faraday tubes on the end of the conductor away from the point (Chattock, Phil. Mag. Aug. 1910). In an arc there are no free charges on the rear of the pole, so the Faraday tubes are concentrated in the space between it and the opposite electrode. It is worth noting that even with a high potential discharge we obtain an accurate balance if we arrange to concentrate the tubes of force on the pointed side of the electrode. I tried the following experiment:—A pointed rod, delicately pivoted, was connected to the negative pole of a not very powerful Wimshurst machine, and a plate, about 5 cm. in diameter connected to the positive terminal was brought near it. When the plate was within 2 or 3 cm. of the point the latter was on the whole stationary (though small fluctuations were observed; sometimes a very faint repulsion, occasionally a rather stronger attraction, due either to air-currents or to fluctuations in the working of the machine). Only when the distance exceeded about 4.5 cm. did the repulsion usually

associated with a point discharge become manifest. The critical distance varied, I think, with the potential attained by the point.

(c) Professor Tyndall suggests as another reason for an unbalanced pressure that there is lack of symmetry whenever "the drag of the ion on the gas" is unequal to the force imposed upon it by the electric field; in particular he argues that, since an ion starting from rest near a pole does not acquire full speed immediately, its "suction" on the electrode it is leaving is proportionately reduced, and consequently a backward pressure may prevail. But surely, if we subscribe to the suction idea and terminology (which is questionable), we ought to take into account the fact that such ions will go on "sucking" longer than if they instantaneously acquired their viscous velocity; the total suction will be the same whether or not it takes an appreciable time to reach the steady state, because it depends only upon the total amount of momentum permanently communicated to the vapour molecules by the moving ions.

So it appears to me that there is here no valid cause of departure from a true balance. I am strengthened in this view by the fact that if we do assume that this type of dissymmetry can occasion a lack of balance and account for the observed pressure, we do not, as Tyndall himself has shown, obtain very probable values for the mobilities of the ions taking part in the phenomenon.

But it seems to me unnecessary to insist upon the dissymmetry hypothesis. Professor Tyndall and Mr. Beer explain certain of their observations upon the manometric pressure by the emission of positive and negative thermions from the hot poles, a feature which, in itself, would seem naturally to call for a recoil phenomenon.

Again, while I do not wish to imply that the projection theory is devoid of difficulties, it appears to me that Professor Tyndall's main objection to my theory arises from a misapprehension. Such evidence as I was able to obtain indicated that the particles responsible for the reaction were electrons, and I sought to fit this information into the scheme of the arc outlined in my paper upon "The Consumption of Carbon in the Electric Arc" (Roy. Soc. Proc. A. xcii. p. 122, 1915). From this investigation it seems definite that, near the cathode, electrons must carry either 0 , $\frac{1}{2}$, $\frac{1}{3}$, or all the current. The pressure work limits us to one of the last four alternatives; all of these give values of e/m for the carrier of the order of magnitude associated with the electron rather than with the atom, but it happens that the value

obtained by assuming that $\frac{1}{2}$ the current near the cathode is borne by electrons gives the value agreeing best with the accepted value; and as this choice also seemed preferable for reasons stated in the above paper, it was this view to which I devoted most attention, though I did not, nor do I now, wish definitely to rule out the other alternatives, because the values obtained for e/m depend upon the distribution of the emitted electrons about the axis of the arc; and upon this point we require further information.

Now, all this argument deals with what takes place *at or in the immediate neighbourhood* of the cathode (as reference to pages 132 and 133 of Phil. Trans. Roy. Soc. A. 220, pp. 109–136, 1919, will confirm); but Professor Tyndall seems to have overlooked the force of the words I have here italicised, because his objection is based on his deduction that the number of positive and negative carriers *in the body of the arc* must be in the ratio of their mobilities, which would imply that if the negative carriers are electrons, they must carry 500 times as much current as the positives—practically the whole of the current. As he definitely excludes the region close to the poles from this category, there is no clear disagreement between our views. It seems to me certain that there will be intense ionization where the projected electrons meet the vapour molecules, especially as they suffer a further fall of some 11·6 volts just outside the cathode, possibly within their mean free path, and therefore that there should be liberated a sufficient number of electrons to carry the bulk of the current and to conform to the condition laid down by Professor Tyndall as pertaining to the body of the arc.

But I think it important to emphasize that the mechanism of the arc is determined chiefly by what goes on at the poles; it does not lead us far if we are content to treat it simply as a mass of gas between two electrodes. The clue to the mechanism of the carbon arc lies in the fact that for each carbon atom which is lost from the cathode of a very short arc, or a long one if extraneous losses are excluded, four electronic charges, or their equivalent, cross the arc-gap. Add to this the facts that the nature of the surrounding gas is of vital importance—we know, for example, that the arc depends for its existence upon interactions between the gas and the material of the poles,—that the maintenance of a hot cathode is essential, and that a certain minimum potential must be maintained across the terminals, depending to some extent upon the temperature we allow the anode to reach, and we have the necessary foundation upon which to erect our theory of the arc.

I do not think we can get away from the four main alternatives enumerated in the paper to which I have referred ; what we must do—what I have endeavoured to do—is to choose the view which fits the new information provided by the reaction observations. I venture to think that Professor Tyndall's contention has not rendered my explanation less probable ; there is nothing contrary to my theory in the manometric pressure-arc length curves upon which he has based his objection.

(2) *The evaporation of carbon atoms from the poles.*

Professor Sellerio, somewhat naively disclaiming any intention of dealing conscientiously with the problem, disregards all other alternatives, and considers that the observed pressure is the reaction consequent upon the evaporation of carbon atoms, a hypothesis which I had previously examined and rejected. Sellerio has, however, recalculated the reaction to be expected on new assumptions, and maintains that the result is substantially in agreement with observation. He dissents from my view that the carbon atoms upon evaporation issue with velocities of the order of magnitude of their atomic speeds appropriate to the temperature of the arc—that is to say, of boiling carbon. He gives reasons for preferring a velocity only $1/500$ to $1/1000$ of this, but his argument is based upon the erroneous supposition that the vapour is saturated upon emission. Some interesting spectrograms of a spark discharge were taken some years ago by Dr. Royds (Phil. Trans. Roy. Soc. 1908) upon a moving film ; each spectrum line was curved like a streamer, whose inclination was a measure of the velocity of the material as it crossed the gap. These velocities I find to be of the same order of magnitude as the atomic velocities calculated on the assumption that the poles are at the boiling-point of the material of which they are composed. Other evidence to the same effect will be found in a paper recently presented to the Editors of this Magazine.

Furthermore, as I hinted in a previous paper⁽⁴⁾, no investigation of the evaporative reaction is complete which does not take into account the interaction of the projected material with the surrounding vapour. This I have recently attempted to do, and find that the reaction R may be simply calculated from the approximate expression $R = (Dv)^2 / 2\Pi A$ if the loss of weight D in gms. per second is small ; here Π is the external pressure, A the area from which the discharge occurs, and v the velocity of projection. Applying this to the 10 amp. 6 mm. arc, we have for the cathode $A = 0.096 \text{ cm.}^2$ (Sellerio) ; D is obtained from our previous

estimate of the carbon loss, 8.5×10^{-4} gm. per sec., of which, however, 66 per cent. occurs from the sides of the carbon and contributes nothing to the reaction; the remainder, 3.1×10^{-4} gm., is the value of D . This gives R (cathode) = .04 dyne. Similarly for the anode, even if we suppose half the total loss to take place from the crater, which is an overestimate, we find R (anode) = .07 dyne. These values are far too small to account for the observed pressure, namely 2.18 and 2.10 dynes respectively.

Even if we were to suppose that the whole loss of carbon assists in producing the reaction, and that it all takes place from the small areas upon the poles from which the arc springs, the corresponding forces would be .33 and .29 dyne respectively, still smaller than the observed values; we have, moreover, the contrary evidence that the forces upon the poles remain constant or diminish to a minimum value as the arc length increases, whereas the total loss of carbon increases to a maximum for both poles.

We calculated⁽³⁾ our value of e/m on the assumption that the projected material did not interfere appreciably with the momentum delivered to the poles by the vapour of the arc—whose undisturbed arrival should provide the ordinary atmospheric pressure upon it,—and found that e/m was of the order of magnitude associated with the electron. This means that the electrons do not to any large extent impart momentum to the vapour molecules as they pass through the arc; when they ionize the vapour, their momentum is in the main handed on to the electrons to which they give rise. A small loss of momentum would not, however, appreciably affect the calculated order of magnitude of e/m .

On the other hand, if we suppose that the projected material does interfere with the external atoms, we must substitute for our equation (1) (Phil. Trans. Roy. Soc. A. 220. p. 131, 1919) the expression

$$\sqrt{3}p = (mvr)^2/2\Pi A,$$

which gives us

$$e/m = VC^2/\sqrt{3}\Pi Ap,$$

which for the cathode leads to $e/m = 1690$, which is reasonably close to the value of e/m for a carbon atom carrying two electronic charges, namely 1600.

The corresponding value for the velocity v is 1.43×10^6 cm./sec., which is some 5 times greater than the atomic velocity, 2.97×10^5 cm./sec., for carbon vapour at 4000°C . I do not wish to state definitely that this is an impossible

value, since a few of the lines for metals measured by Royds (*loc. cit.*) gave values for v about 5 times as great as the velocity of atomic agitation at the boiling-point, but in these cases there were always other and stronger lines which provided values nearly equal to the temperature velocities. Still, the matter is in an interesting stage; it would open up new difficulties if the vapour in the arc were to receive so much of the momentum of the projected material that only a few per cent. reached the opposite pole, or were effective in producing a recoil upon the pole from which the material was originally derived.

I therefore submit that in the present state of our knowledge the evidence is against the evaporation of carbon being the main cause of the phenomenon, though I do not think it quite negligible. Indeed, in the particular state of the iron arc which I characterized as turbulent, as distinct from the normal quiescent arc, I believe it plays the predominant part. Even in the case of the carbon arc, more exact information regarding the sizes of the hot spots might cause us to revise our conclusions. We can, however, only deal with the evidence before us.

(3) *On the relationship between the manometric and mechanical pressures.*

One hesitates to criticize the deductions made by an observer from his own experiments, but I think it important to suggest, though I scarcely expect Prof. Tyndall to agree with me, that it does appear from his and Mr. Beer's important experiments⁽⁷⁾ upon the manometric pressure within the arc that this arises from the same cause as that which produces the mechanical reaction upon the poles, namely the projection of particles from the cathode.

If we accept electronic projection from the cathode, what manometric pressures should we expect at the two poles? At the cathode, if the hole is central and small enough to be completely within the hot spot, there will be high-speed electrons projected from the walls of the tube more or less normally, and these will occasion a positive pressure there; if the hole is not central or too large to be completely covered, we should expect the electrons projected from the end to impart some at least of their momentum to the gas molecules, which will thus be withdrawn from the tube leading to the manometer, causing it to record a reduced pressure. At the anode the arrival of negative ions should occasion an increase of pressure, and, as the hot spot is large, this would be

observed with much larger holes than could be used in the cathode.

This is precisely what Tyndall and Beer observed. They also found that, when definite results were obtainable, the manometric pressure increased with the current just as the mechanical pressure does, and that the variation of hydrostatic pressure at the anode agreed with our Series B curves. In addition they occasionally noted a very minute negative pressure at the anode when the current was very small and the hole large and non-central; this I should ascribe either to convection currents, which were certainly not negligible in my experiments, or, as Tyndall and Beer regard it, to the effect of thermionic projection there.

Nor is the magnitude of the manometric effect out of keeping with the view that it is due to an electronic discharge from the cathode*. Taking, for obvious reasons, the *maximum* positive pressure observed in a hole in the cathode, namely 24.7 dynes per sq. cm. for a current of 13.5 amps., which is equivalent to $24.7 \times 10, 13.5$ dyne/cm.² for a 10 amp. arc, we see that, since the area of the hot spot is 0.096 cm.², according to Sellerio, the reaction upon the whole arc should be $24.7 \times 0.096 \times 10, 13.5$ or 1.76 dyne, which is in reasonable agreement with the 2.1 dynes which we observed; it is certainly of the right order of magnitude.

The manometric pressure at the anode observed by Tyndall and Beer was 8.8 dyne cm.² for a current of 10 amperes (measured from their curve "D"). The area of the crater being 0.31 cm.² (Sellerio), the reaction to be expected is $8.8 \times 0.31 = 2.73$ dynes; this is somewhat in excess of the mechanical pressure observed by Burnham, Davis, and myself, but remarkably close considering the difficulties of estimating the size of hole and of crater, and considering also that the presence of the hole must somewhat modify the conditions within the arc.

We note further that the "suction" at the cathode was observed by Tyndall and Beer to be much less numerically than the positive manometric pressure at the anode, the ratio for a 10-ampere arc being rather less than 1 to 4. This is in keeping with our view that the bulk of the momentum is conveyed across the arc to the anode without imparting it to the vapour molecules.

Dundrennan, Glenelg,
South Australia,
Feb. 1923.

* The approximate quantitative agreement was first pointed out by Sellerio⁽⁹⁾ though he did not suggest that the effects were otherwise related.—D. G.

CXX. *A Theory of the Abnormal Cathode Fall.* By The Research Staff of the General Electric Co., Ltd., London *.
(*Work conducted by J. W. RYDE.*)

Summary.

A THEORY of the abnormal cathode fall is given, according to which conduction in the dark space is closely analogous to that in a high vacuum between a plane thermionic cathode and plane anode. According to the theory, the width of the dark space with given current and voltage should be determined by the atomic weight of the gas and universal constants.

The theory is compared with the measurements of Aston and of Aston and Watson. The relatively small divergence between the simple theory and experiment can be removed, partially at least, by taking into account the electrons liberated at the cathode, information concerning which is given by Cheney's measurements, and the collisions of the positive ions with neutral molecules.

But it seems difficult to reconcile the theory with Aston's determination of the variation of the electric field through the dark space.

ALL theories of the cathode fall with which we are acquainted assume that it is determined largely by collisions of the positive ions with neutral molecules within the cathode dark space. The assumption is made either when it is assumed that the velocity of the ions at any point is proportional to the field there, or when it is assumed that the cathode fall is determined by the ionization potential.

So far as the normal cathode fall is concerned (and it is to the normal fall that such theories have usually been directed) the assumption is probably correct. But in a recent paper we have shown that there is some reason for believing that it is not correct in the abnormal fall. The cathodic disintegration, which increases so very greatly in the passage from the normal to the abnormal fall, seems explicable only if, when the fall is abnormal, the positive ions arrive at the cathode with nearly the full velocity corresponding to the fall; their velocity has not been greatly reduced by collisions. Accordingly, it seems worth while to proceed to the other extreme and to discuss the abnormal cathode fall on the assumption that there are no collisions. Doubtless the assumption is not exactly true, but it may be

✦ Communicated by the Director.

possible to introduce the effect of the collisions as a small correction to a theory based on ignoring them.

It is known that the intensity of the field is very small at the boundary between the dark space and the cathode glow. Let us assume that the division between the dark space and the glow is a definite plane, parallel to the plane cathode, and that in this plane the field is zero. Physically, the assumption is possible, for it implies that the number of positives disappearing by recombination in the glow is very large compared with the number dragged out of it to the cathode by the field; and the luminosity of the glow indicates that recombination is proceeding rapidly. Now, if these assumptions are made, the problem of determining the relation between the current through the dark space, the potential difference across it, and the distance between its boundaries is precisely analogous to that of determining the corresponding relation for a plane thermionic cathode in a high vacuum. To the electrons in the thermionic case correspond the positive ions, to the hot cathode at which $dV/dx=0$ corresponds the boundary between the negative glow and dark space, and to the cathode corresponds the anode. It is well known that the relation is given by

$$di^{1/2} = kV_1^{3/4}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where

$$k^4 = \frac{2}{81\pi^2} \frac{e}{m_1}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Here i is the current, d the distance, and V_1 the potential difference between the electrodes, e and m_1 , the charge and mass of the carriers, which are now the positive ions of the gas in the discharge-tube, and not electrons.

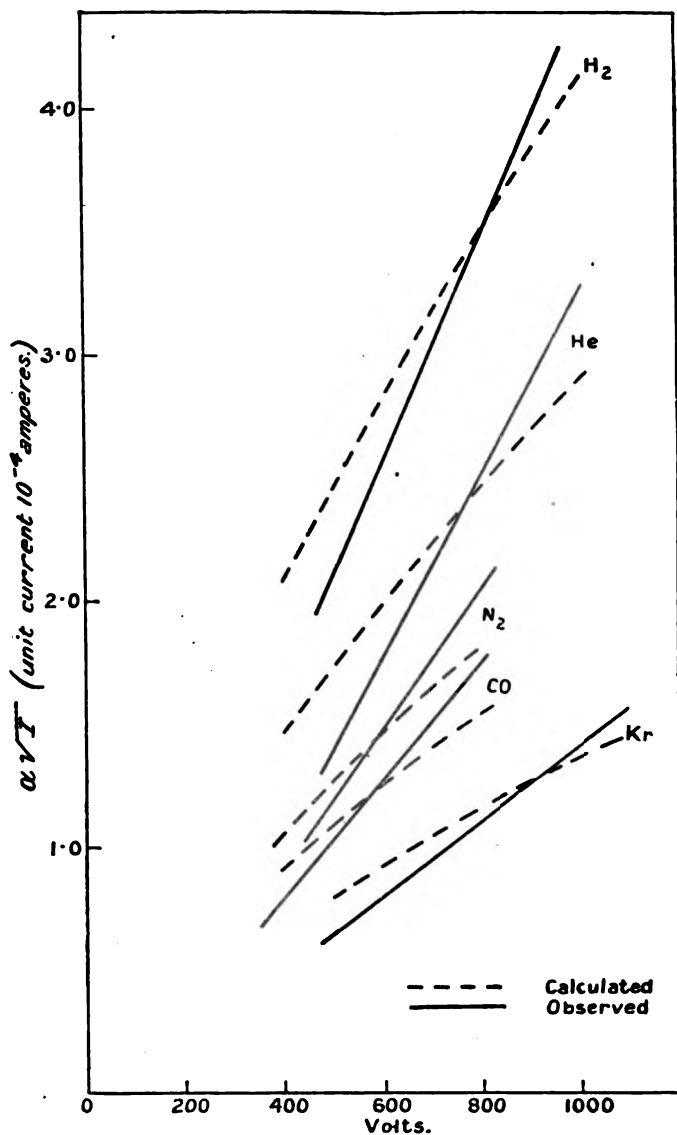
The relation between V_1 , i , d has been determined experimentally for a number of gases by Aston and Aston and Watson*, who expressed their results by the empirical formula

$$di^{1/2} = k_1(V-G), \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

which differs in form from (1) only by the substitution of $V-G$ for $V^{3/4}$, where G and k_1 are constants, determined by the gas and the material of the cathode. We have calculated the relation between $di^{1/2}$ and V_1 , first from the empirical equation (3), which represents directly the experimental results with aluminium electrodes (see p. 1155), and second from our equation (1), which contains, beyond the

* F. W. Aston, Proc. Roy. Soc. A. lxxix. p. 80 (1907); F. W. Aston and H. E. Watson, *ib.* A. lxxxvi. p. 168 (1912).

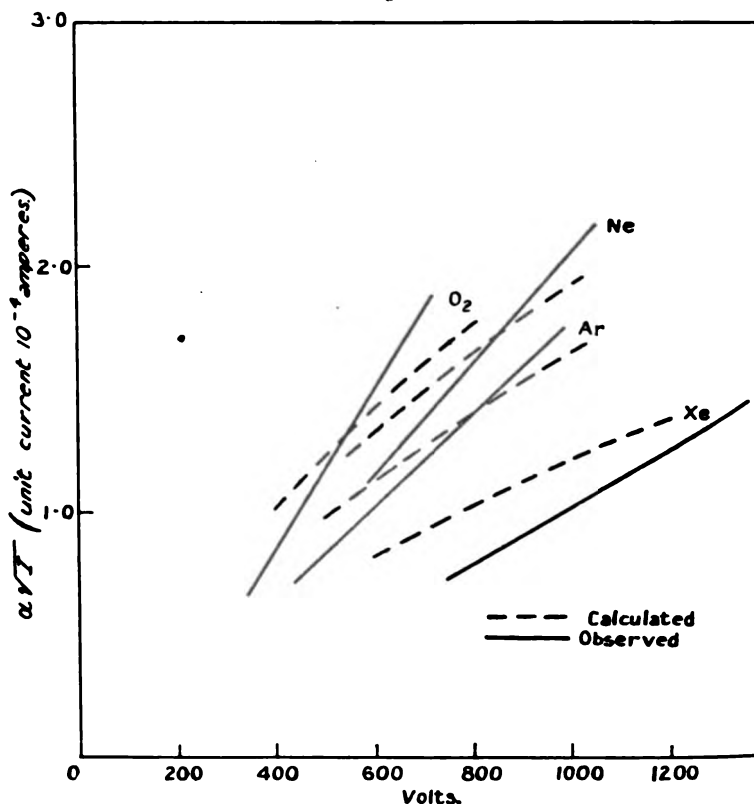
Fig. 1.



atomic weight of gas, nothing but universal constants. The results are indicated in figures 1, 2, where the full lines give the observed results ; the dotted lines the calculated results.

It is obvious at once that observation and calculation do not wholly agree; and we do not pretend that they do or suggest that they ought to agree. But we would point out that they agree in order of magnitude, and that the relation between the observed and calculated lines is of the same nature for all the gases. They all cross at about the

Fig. 2.



same angle and in the same region of voltage. We draw the conclusion that in general outline our theory is correct, and that the remaining discrepancy is due to some factors of minor importance that we have neglected.

There are two such factors. First, there are the electrons liberated by the positives when they impinge on the cathode; second, there are collisions of the positive ions, and perhaps of the electrons, with the neutral molecules. We will discuss them in turn.

The electrons from the cathode will have two effects on the relation in question. They will carry some of the current, and, by neutralizing partially the space charge, they will permit more positives to cross under the same field. It is easily shown that the second effect is wholly negligible. For, with the notation usual in the analogous case and putting $V=x=0$ at the boundary between dark space and glow, we have

$$\frac{d^2V}{dx^2} = -4\pi e(n_+ - n_-), \quad (4)$$

$$i = e(n_+v_1 + n_-v_2), \quad (5)$$

$$\frac{1}{2}m_1v_1^2 = eV, \quad \frac{1}{2}m_2v_2^2 = e(V_1 - V). \quad . . (6)$$

If each positive ion causes the emission of q electrons from the cathode,

$$n_-v_2 = qn_+v_1. \quad (7)$$

Proceeding in the usual manner we find

$$\left(\frac{dV}{dx}\right)^2 = \frac{ai}{q+1} \{V^{1/2} + b(V_0 - V)^{1/2} - bV_0^{1/2}\}, \quad . (8)$$

where

$$a = 8\sqrt{2}\pi\left(\frac{m_1}{e}\right)^{1/2}, \quad (9)$$

$$b = q\left(\frac{m_2}{m_1}\right)^{1/2}. \quad (10)$$

Now, q is not greater than 0.1, $\frac{m_2}{m_1}$ not greater than .0006; hence b is not greater than .002. But b is the maximum ratio of the sum of the last two terms in the bracket to the first. It is clear then that b may be neglected and that the only appreciable effect of the electrons from the cathode is represented by the q outside the bracket. In other words, though these electrons carry an appreciable fraction of the current, they do not alter the field appreciably.

Accordingly, the only change in (1) necessary is the substitution of $i/(q+1)$ for i , so that now

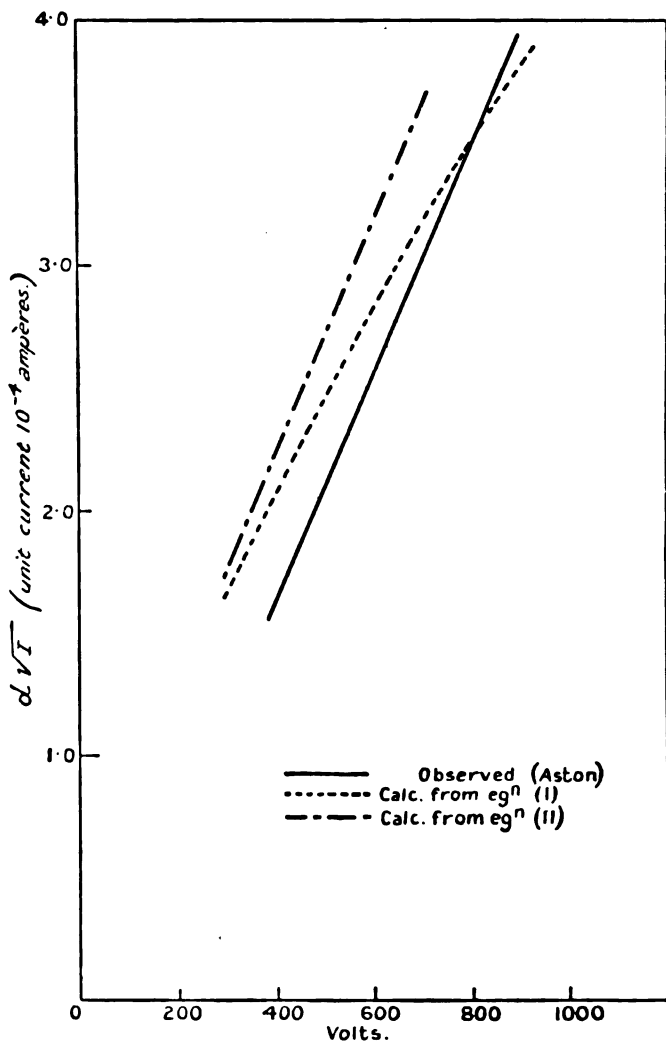
$$di^{1/2} = k(q+1)^{1/2}V_1^{3/4}. \quad (11)$$

q can be estimated from the observations of Cheney*. It is determined by the speed and nature of the ions and of the material of the cathode. Unfortunately, Cheney's results refer only to lithium, potassium, and rubidium ions; but it appears from them that q for hydrogen should not be very

* W. L. Cheney, Phys. Rev. x. p. 335 (1917).

different from that for lithium. Using Cheney's value of q for lithium and an aluminium cathode, we may recalculate from (11) the relation for hydrogen and the same cathode.

Fig. 3.—Hydrogen with Aluminium Cathode.



and compare it with Aston's measurement. In fig. 3 the full line is that observed, the dotted curves those calculated from (1) and (11).

It will be seen that the introduction of q makes the

observed and calculated lines almost parallel, but the latter is definitely higher. It is unfortunate that Aston's* measurements on cathodes other than aluminium were made without guard-rings, and are therefore not comparable with the theoretical equations, and that q is not known for other positive ions. But qualitatively the influence of the material of the cathode and of the nature of the ions is always in the direction indicated by (11) and by Cheney's values of q .

It remains to be explained why the values of $di^{1/2}$ given by (11) are uniformly greater than those observed. The discrepancy is doubtless partly due to the fact that Aston's V is the difference of potential between anode and cathode, while ours is that between negative glow and cathode, and is therefore slightly smaller. But the presence of the neutral molecules must be taken into account. The electrons produced by ionization will not be important, for they are few in number compared with those from the cathode. However, the loss of energy of the positive ions at collisions may be appreciable. It will produce an effective decrease of V or increase of m_1 , and will therefore bring the calculated line nearer to the experimental. But we have not succeeded in making an estimate of their effect sufficiently accurate to enable a numerical comparison to be made. We hope, however, in the future to throw further light on the matter by determining by means of sputtering with what velocity the positive ions actually strike the cathode.

One further discrepancy remains. Aston found that in the dark space dV/dx was proportional to x ; according to (8) it should be proportional to $x^{1/3}$. No explanation can be offered at present; reduction of the energy of the positive ions by collisions with neutral molecules must change somewhat the distribution of the field, but it seems difficult to believe that it could distort it so completely as Aston's measurements indicate without at the same time changing the currents so as to remove all agreement between experiment and theory. However, whatever may be the solution of this difficulty, we feel that sufficient evidence has been produced that with abnormal cathode fall, the width of the dark space is determined mainly by the atomic weight of the gas, and that the positive ions arrive at the cathode with very nearly the velocity corresponding to the full cathode fall.

We take this opportunity of correcting an error in a previous paper, *Phil. Mag.* xlv. pp. 99-112, 1923. On p. 102, l. 3, for " $m'/C' = \text{constant}$ ", read " $m'C' = \text{constant}$ ".

* F. W. Aston, *Proc. Roy. Soc. A.* lxxxvii. p. 437 (1912).

CXXI. *Extended Application of the Principle of Stationary Phase in Wave-Motion Problems.* By GEORGE GREEN, D.Sc.*

IN a former paper under the title "On Group-Velocity and on the Propagation of Waves in a Dispersive Medium" †, the theory of group-velocity is discussed from the standpoint of the late Lord Kelvin's paper of 1887, "On the Waves produced by a Single Impulse in Water of any Depth, or in a Dispersive Medium." The theory of group-velocity contained in this paper is essentially the same as the principle of "stationary phase" frequently employed in optical and other waves problems. This principle is illustrated in the above paper in the evaluation of the integral

$$\xi = \frac{1}{2\pi} \int_0^\infty dk \cos [k\{x - Vt\}] : V = f(k), \quad . \quad . \quad (1)$$

expressing the effect at any point x at time t of an impulse delivered at the origin at time zero in any dispersive medium. For each Fourier train represented in the above integral by a definite value of k , we have the wave-length $\lambda = \frac{2\pi}{k}$, the wave-velocity $V = f(k)$, and the phase $\phi = [k(x - Vt)]$ at point x at time t . The condition that the phase of the constituent Fourier trains is stationary in the neighbourhood of a definite value k_0 at point x at time t is

$$\frac{d\phi}{dk} = x - \frac{d(kV)}{dk} t = 0, \quad \text{or} \quad x = \{f(k_0) + k_0 f'(k_0)\} t. \quad . \quad (2)$$

Thus the point of the medium at which the wave-length $\frac{2\pi}{k_0}$ predominates changes its position with velocity, $U = \{f(k_0) + k_0 f'(k_0)\}$, where U is the group-velocity corresponding to wave-length $\frac{2\pi}{k_0}$.

According to the principle of "stationary phase," the wave-trains which contribute effectively to the resultant displacement of the medium ξ , at point x at time t , are those included in a narrow range of k on either side of k_0 : and the phase ϕ within this range may be represented accurately by

* Communicated by the Author.

† Proc. R. S. E. vol. **xx**. (1909).

a few terms of the series

$$\begin{aligned}\phi &= [k\{x - Vt\}] = k_0\{x - f(k_0)t\} + (k - k_0) \frac{d\phi}{dk_0} + \frac{(k - k_0)^2}{2!} \frac{d^2\phi}{dk_0^2} \\ &\quad + \frac{(k - k_0)^3}{3!} \frac{d^3\phi}{dk_0^3} + \text{etc.} \\ &= a_0 + \frac{b_0}{2!} \sigma^2 + \frac{c_0}{3!} \sigma^3 + \text{etc.,} \quad . \quad . \quad . \quad (3)\end{aligned}$$

in which $\frac{d\phi}{dk_0} = 0$, and we have put σ instead of $k - k_0$.

Outside the effective range the phase varies rapidly with k , and the quantity to be integrated consists of a large number of positive and negative parts whose total effect is very small. Within the effective range of k on either side of k_0 , the number of terms of the series required to represent the phase ϕ with sufficient accuracy depends upon the relative values of the successive terms. The case treated by Lord Kelvin in the paper above referred to, and by later writers also, is that in which $\frac{d^2\phi}{dk^2}$ is large compared with any term coming after it. The evaluation given by Lord Kelvin is therefore restricted in its application to certain definite ranges of x and t within which the term $\frac{d^3\phi}{dk^3}$ is exceedingly small compared with $\frac{d^2\phi}{dk^2}$. The evaluation given by Lord Kelvin is contained in the statements

$$\begin{aligned}\xi &= \frac{1}{2\pi} \int_0^\infty dk \cos \phi = \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\sigma \cos \left[a_0 + \frac{b_0}{2!} \sigma^2 \right] \\ &= \frac{1}{(\pm 2\pi b_0)^{\frac{1}{2}}} \cos \left(a_0 \pm \frac{\pi}{4} \right), \quad . \quad . \quad (4)\end{aligned}$$

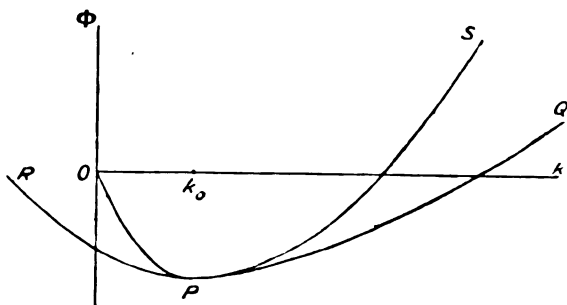
the negative sign being taken when b_0 is negative.

The process here employed virtually consists in replacing the curve OPQ in fig. 1, representing the true phase over the whole range of k from zero to infinity, by a curve, RPS, which coincides with the true phase-curve only in the immediate neighbourhood of k_0 , the point at which the phase is stationary for variations in k . On account of the rapid variation in phase on the assumed phase-curve beyond a very small range on either side of k_0 , the contribution to the total value of the integral depending on these parts of the curve is very small, just as in the case of the true phase-curve. The same reasoning justifies the infinite limits in the case of

the auxiliary curve, provided k_0 is not itself a very small quantity. When k_0 is a small quantity, the lower limit of the integral is not $-\infty$ but $-k_0$ if a slightly better approximation than that given in (4) is required.

The evaluation given above applies to the case where, at point x at time t , the phase-curve has one point of stationary phase. The range of values of x and t to which the result applies depends on the closeness of the agreement between the auxiliary phase-curve and the true phase-curve over a considerable range of values of k . This agreement between the two curves near the stationary point is, of course, improved

Fig. 1.

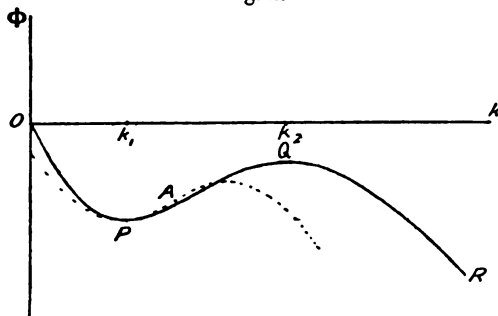


by the inclusion of the term $\frac{d^3\phi}{dk_0^3}$ in the series, but the new auxiliary curve is now of a different type from the original curve, being a curve with a point of inflexion and two stationary points, and it is accordingly unsuitable for use over the full range of integration.

When however the phase-curve itself has two points, k_1 and k_2 , at which the phase is stationary as in the curve OPQR of fig. 2, the third term in the series must be included in order to obtain the necessary agreement between the auxiliary phase-curves and the true phase-curve. In this case the $\frac{d^3\phi}{dk^3}$ term is not small compared with the $\frac{d^2\phi}{dk^2}$ term, and may become the predominant term. This occurs when the two roots of $\left(\frac{d\phi}{dk} = 0\right)$ become very close, or pass into coincidence when therefore $\frac{d^2\phi}{dk^2}$ becomes zero altogether. The intention of the present paper is to discuss fully the

evaluation of ξ when the $\frac{d^3\phi}{dk^3}$ term is included in the expression for the auxiliary phase-curve. The discussion applies to all cases where there are maxima or minima of the group-velocity, and contains the extension referred to by Lord Kelvin at the close of his paper, where he remarks "The working out of our present problem for this case, or any case in which there are either minimums or maximums, or both maximums and minimums, of wave-velocity, is particularly interesting, but time does not permit of its being included in the present communication."

Fig. 2.



Let us take the curve represented in fig. 2 to be the true phase-curve, k_1 and k_2 being the two stationary points at which $\frac{d\phi}{dk} = 0$. The auxiliary phase-curve exactly agreeing with this curve in the neighbourhood of k_1 is given by

$$\phi_1 = a_1 + \frac{b_1}{2!} \sigma^2 - \frac{c_1}{3!} \sigma^3, \quad \dots \dots (5)$$

and that agreeing with the true curve in the neighbourhood of k_2 is given by

$$\phi_2 = a_2 - \frac{b_2}{2!} \sigma^2 - \frac{c_2}{3!} \sigma^3. \quad \dots \dots (6)$$

The dotted curve shown in the figure represents the auxiliary curve at k_1 . When k_1 and k_2 are nearly equal, it follows from Taylor's expansion that all three curves agree over the full range between k_1 and k_2 , but in general, with $k_2 - k_1$ large, the agreement of each curve with the true phase-curve ceases to be sufficiently good beyond the point of inflexion. On the auxiliary curve at k_1 , the point of inflexion occurs when $(k - k_1)$ has the value $+\frac{b_1}{c_1}$ and the

curve itself is symmetrical about its point of inflexion. Similarly, on the auxiliary curve at k_2 the point of inflexion occurs when $k-k_2$ has the value $-\frac{b_2}{c_2}$, and this curve also is symmetrical about its own point of inflexion. If now we employ the auxiliary phase-curve for k_1 for integration up to its point of inflexion and the auxiliary phase-curve for k_2 for integration from its point of inflexion outwards to infinity, we shall obtain a value for the complete integral similar to that obtained by Lord Kelvin for the case of a single point of stationary phase on the true phase-curve. When $\frac{b_1}{c_1}$ is exceedingly large, the point of inflexion A on the first auxiliary curve at k_1 is far removed from k_1 , and the whole integration in which the k_1 curve is employed corresponds exactly to the case dealt with by Lord Kelvin except in this, that the auxiliary phase-curve used contains the additional terms depending upon c_1 . In this case also the same remark applies to the integration in which the k_2 auxiliary phase-curve is employed.

According to the above an approximate value for the integral appearing in (1) may be obtained by writing

$$\xi = \frac{1}{2\pi} \int_{-k_1}^{+\frac{b_1}{c_1}} \cos \phi_1 d\sigma + \frac{1}{2\pi} \int_{-\frac{b_2}{c_2}}^{\infty} \cos \phi_2 d\sigma = \xi_1 + \xi_2, \quad (7)$$

where ϕ_1 and ϕ_2 are given by (5) and (6) respectively. By means of the substitution

$$\frac{\pi}{2} w^3 = \frac{c_1}{3!} \left(\sigma - \frac{b_1}{c_1} \right)^3$$

in the first of the above integrals, and of the substitution

$$\frac{\pi}{2} w^3 = \frac{c_2}{3!} \left(\sigma + \frac{b_2}{c_2} \right)^3$$

in the second, each of the auxiliary phase-curves is referred to an origin at its point of inflexion, and (7) is transformed into

$$\begin{aligned} \xi = & \frac{1}{2\pi} \left\{ \frac{\pi}{2} \cdot \frac{3!}{c_1} \right\}^{1/3} \int_{-\infty}^0 dw \cos \left[\left(a_1 + \frac{1}{3} \cdot \frac{b_1^3}{c_1^3} \right) - \frac{\pi}{2} (w^3 - m_1 w) \right] \\ & + \frac{1}{2\pi} \left\{ \frac{\pi}{2} \cdot \frac{3!}{c_2} \right\}^{1/3} \int_0^{\infty} dw \cos \left[\left(a_2 - \frac{1}{3} \cdot \frac{b_2^3}{c_2^3} \right) - \frac{\pi}{2} (w^3 - m_2 w) \right], \\ & \dots \quad (8) \end{aligned}$$

where

$$\alpha = \left\{ \frac{2}{\pi} \cdot \frac{c_1}{3!} \right\}^{1/3} \left(k_1 + \frac{b_1}{c_1} \right).$$

$$m_1 = \frac{1}{3} \left(\frac{2}{\pi} \right)^{2/3} \left(\frac{3!}{c_1} \right)^{4/3} \left(\frac{b_1}{2!} \right)^2, \quad m_2 = \frac{1}{3} \left(\frac{2}{\pi} \right)^{2/3} \left(\frac{3!}{c_2} \right)^{4/3} \left(\frac{b_2}{2!} \right)^2.$$

When the points of stationary phase coincide at k_1 , we have $a_1 = a_2$, $b_1 = b_2 = 0$, $c_1 = c_2$, $m_1 = m_2 = 0$, and

$$\xi = \frac{1}{2\pi} \left\{ \frac{\pi 3!}{2 c_1} \right\}^{1/3} \int_{-\alpha}^{\infty} dw \cos \left[a_1 - \frac{\pi}{2} w^3 \right]. \quad (9)$$

When α is assumed to be very large, as in the cases treated by Lord Kelvin, we may put $\alpha = \infty$, and then we have for the special case considered in (9),

$$\xi = \frac{1}{2\pi} \left\{ \frac{\pi 3!}{2 c_1} \right\}^{1/3} \cos a_1 \int_{-\infty}^{+\infty} dw \cos \frac{\pi}{2} w^3, \quad (10)$$

which is the same as a result given by the late Lord Rayleigh* and by T. H. Havelock†.

For the complete evaluation of ξ in (8) we require the values of the integrals

$$\int_0^a dw \cos \frac{\pi}{2} (w^3 - mw) \quad \text{and} \quad \int_0^a dw \sin \frac{\pi}{2} (w^3 - mw)$$

for values of α finite and infinite‡. Each of these integrals is a function of m , $I(m)$, such that $I(0)$ and its derivative $I'(0)$ may be regarded as known, being defined by well-known integrals. Each integral also, regarded as a function of m , satisfies a differential equation of the form

$$\frac{d^2 I}{dm^2} + \left(\frac{\pi}{2} \right)^2 \cdot \frac{m}{3} I = C \text{ (a constant):} \quad (11)$$

and the values of the above integrals are readily obtained by first writing down the complete solution of this equation and then determining the two arbitrary constants by means of the known values of $I(0)$ and $I'(0)$. In the present paper we shall put down the results only for the case of $\alpha = \infty$, as the corresponding results for α finite can be readily written

* Scientific Papers, vol. vi. p. 10.

† Phil. Trans. lxxxi. (1908).

‡ The cosine integral has been evaluated in the form of a series by Stokes, who has also established the convergency of the integrals (Mathematical Papers, vol. ii. p. 329). The cosine integral has also been evaluated by Wirtinger, in 'Zwei Bemerkungen zu Airy's Theorie des Regensbogens,' by the method employed in the present paper.

down by the method employed here when we come to discuss particular problems in which these integrals are required. The complete solution of equation (11) is given by

$$I(m) = A m^{1/3} J_{-1/3} \left\{ \pi \left(\frac{m}{3} \right)^{3/2} \right\} + B m^{1/2} J_{1/3} \left\{ \pi \left(\frac{m}{3} \right)^{3/2} \right\} + C F(m), \quad \dots (12)$$

where

$$F(m) = \frac{m^2}{1 \cdot 2} - \frac{p m^5}{1 \cdot 2 \cdot 4 \cdot 5} + \frac{p^2 m^8}{1 \cdot 2 \cdot 4 \cdot 5 \cdot 7 \cdot 8} - \text{etc.};$$

$$\text{and } p = \left(\frac{\pi}{2} \right)^2 \cdot \frac{1}{3} \cdot \dots (13)$$

For the integral $\int_0^\infty dw \cos \frac{\pi}{2} (w^3 - mw)$;

$$C=0, \quad I(0) = \frac{1}{2} \frac{1}{\sqrt{3}} \left(\frac{2}{\pi} \right)^{1/3} \Gamma \left(\frac{1}{3} \right), \quad I'(0) = \frac{1}{2} \frac{1}{\sqrt{3}} \left(\frac{\pi}{2} \right)^{1/3} \Gamma \left(\frac{2}{3} \right).$$

For the integral $\int_0^\infty dw \sin \frac{\pi}{2} (w^3 - mw)$;

$$C = -\frac{\pi}{6}, \quad I(0) = \frac{1}{6} \left(\frac{2}{\pi} \right)^{1/3} \Gamma \left(\frac{1}{3} \right), \quad I'(0) = -\frac{1}{6} \left(\frac{\pi}{2} \right)^{1/3} \Gamma \left(\frac{2}{3} \right).$$

The values of these integrals are accordingly given by

$$\int_0^\infty dw \cos \frac{\pi}{2} (w^3 - mw)$$

$$= \frac{\pi}{3} \cdot \left(\frac{m}{3} \right)^{1/2} \left[J_{-1/3} \left\{ \pi \left(\frac{m}{3} \right)^{3/2} \right\} + J_{1/3} \left\{ \pi \left(\frac{m}{3} \right)^{3/2} \right\} \right], \quad \dots (14)$$

and

$$\int_0^\infty dw \sin \frac{\pi}{2} (w^3 - mw)$$

$$= \frac{\pi}{9} \cdot m^{1/2} \left[J_{-1/3} \left\{ \pi \left(\frac{m}{3} \right)^{3/2} \right\} - J_{1/3} \left\{ \pi \left(\frac{m}{3} \right)^{3/2} \right\} \right] - \frac{\pi}{6} F(m).$$

$$\dots (15)$$

The expressions which we have obtained for the sine and cosine integrals are useful for calculation when the quantity m is small in value. When m is large we can employ the asymptotic expressions for the Bessel's functions, but an asymptotic value for the function $F(m)$ is also required,

and it can be obtained by means of the integral

$$\int_0^{\infty} dw e^{-\frac{\pi}{2}(w^3+mw)}$$

If we first expand $e^{-\frac{\pi}{2}mw}$ and integrate term by term; and if we expand $e^{-\frac{\pi}{2}w^3}$ and then integrate term by term; we obtain two different expressions for the value of the integral:

$$\begin{aligned} \int_0^{\infty} dw e^{-\frac{\pi}{2}(w^3+mw)} \\ &= \frac{2\pi}{9} m^{1/2} \left[J_{-1/3} \left\{ \pi \left(\frac{m}{3} \right)^{3/2} \right\} - J_{1/3} \left\{ \pi \left(\frac{m}{3} \right)^{3/2} \right\} \right] + \frac{\pi}{6} F(m) \\ &= \frac{\pi}{6} \left(\frac{1}{pm} - \frac{1.2}{p^2 m^4} + \frac{1.2.4.5}{p^3 m^7} - \text{etc.} \right). \quad \dots \quad (16) \end{aligned}$$

Eliminate $F(m)$ from (15) by means of this equality, and we have the asymptotic value for the sine integral given by

$$\begin{aligned} \int_0^{\infty} dw \sin \frac{\pi}{2} (w^3 - mw) \\ &= \frac{\pi}{3} m^{1/2} \left[J_{-1/3} \left\{ \pi \left(\frac{m}{3} \right)^{3/2} \right\} - J_{1/3} \left\{ \pi \left(\frac{m}{3} \right)^{3/2} \right\} \right] \\ &\quad - \frac{\pi}{6p} \left(\frac{1}{m} - \frac{1.2}{pm^4} + \text{etc.} \right). \quad \dots \quad (17) \end{aligned}$$

Taking only the first term of the well-known asymptotic values for the Bessel functions, we find, for m exceedingly large,

$$\begin{aligned} \int_0^{\infty} dw \cos \frac{\pi}{2} (w^3 - mw) &= \frac{2^{1/2}}{(3m)^{1/4}} \cos \left\{ \pi \left(\frac{m}{3} \right)^{3/2} - \frac{\pi}{4} \right\} : \\ \int_0^{\infty} dw \sin \frac{\pi}{2} (w^3 - mw) &= - \frac{2^{1/2}}{(3m)^{1/4}} \sin \left\{ \pi \left(\frac{m}{3} \right)^{3/2} - \frac{\pi}{4} \right\}, \quad (18) \end{aligned}$$

in agreement with a result given by Stokes*.

The above results enable us to evaluate the integrals contained in (8) for the case where $\alpha = \infty$; that is, where k_1 is large, and so to determine ξ . It is interesting to note that

* *Ibid.* p. 341, equation (23).

when m_1 and m_2 become very large the portions of the auxiliary phase-curves employed in the integrations extend to infinity on both sides of the point at which the phase is stationary. Taking for example the second integral in (8), with m_2 very large, we can readily verify that its value is given by

$$\xi_2 = \frac{1}{2\pi} \left\{ \frac{\pi}{2} \cdot \frac{3!}{c_2} \right\}^{1,3} \cdot \cos \left[\left(a_2 - \frac{1}{3} \frac{b_2^3}{c_2^2} \right) + \left\{ \pi \binom{m}{3}^{3/2} - \frac{\pi}{4} \right\} \cdot \frac{2^{1/2}}{(3m)^{1/4}} \right], \quad (19)$$

or, since

$$\pi \binom{m}{3}^{3/2} = \frac{1}{3} \frac{b_2^3}{c_2^2},$$

by

$$\xi_2 = \frac{1}{(2\pi b_2)^{1/2}} \cos \left[a_2 - \frac{\pi}{4} \right], \quad \dots \quad (20)$$

which coincides with the result given by (4) for a phase-curve having one point at which the phase is stationary. When the two stationary points k_1, k_2 are widely separated, we have proved that the result given by (8) is equivalent to the result obtained by applying Lord Kelvin's evaluation given in (4) at each point of stationary phase separately, as already pointed out. By means of (14) and (15), and the corresponding results obtained for α finite, we can accordingly evaluate ξ for all curves of the type shown in fig. 2, whether the points of stationary phase are very near each other or the reverse.

In the general case an auxiliary phase-curve of the type

$$\phi = a + \frac{b}{2!} \sigma^2 + \frac{c}{3!} \sigma^3$$

can only be used to represent a curve with one point of stationary phase over a limited range. Beyond the point of inflexion on the auxiliary curve its form differs entirely from that of the curve it is intended to replace. Similarly, if we take four terms of equation (3),

$$\phi = a + \frac{b}{2!} \sigma^2 + \frac{c}{3!} \sigma^3 + \frac{d}{4!} \sigma^4,$$

to represent a phase-curve having only one point of stationary

phase, the auxiliary phase-curve can only represent the original curve between two points of inflexion on the auxiliary curve. Provided the portion of the auxiliary curve employed is of the same type as the original phase-curve, the results obtained by means of the auxiliary curve are more and more exact as the terms containing higher and higher powers of σ are included in the auxiliary phase-curve. This is well illustrated in the application of the stationary phase principle to derive the asymptotic expressions for the Bessel functions. The first term of this expression has already been derived by the late Lord Rayleigh* by means of the result given in (4). Taking the function,

$$J_n(z) = \frac{1}{\pi} \int_0^\pi d\omega \cos \{z \sin \omega - n\omega\}, \quad \dots \quad (21)$$

we require an expression for its value when z is very large, and n is small compared with z . The phase $\{z \sin \omega - n\omega\}$ is stationary at the value of ω given by $\cos \omega_1 = n/z$, and the auxiliary phase-curve is represented by

$$(z \sin \omega - n\omega) = (z \sin \omega_1 - n\omega_1) - \frac{z \sin \omega_1}{2!} \sigma^2 - \frac{n}{3!} \sigma^3 + \frac{z \sin \omega_1}{4!} \sigma^4, \quad \dots \quad (22)$$

if we include four terms of equation (3). If we put

$$\frac{z \sin \omega_1}{2!} \sigma^2 = y^2,$$

the approximate value of the function (21) is given by

$$J_n(z) = \frac{1}{\pi} \sqrt{\frac{2}{z \sin \omega_1}} \int_{-y_1}^{y_2} dy \cos \{\phi_1 - y^2 - \alpha y^3 + \beta y^4\}, \quad (23)$$

where $\phi_1 = (z \sin \omega_1 - n\omega_1)$,

$$\alpha = \frac{n}{6} \left(\frac{2}{z \sin \omega_1} \right)^{3/2}; \quad \beta = \frac{1}{6z \sin \omega_1};$$

and the values y_1, y_2 corresponding to points of inflexion on the auxiliary phase-curve are given by

$$y_1 = \sqrt{z \sin \omega_1} - \frac{n}{\sqrt{2z \sin \omega_1}} \quad \text{and} \quad y_2 = \sqrt{z \sin \omega_1} + \frac{n}{\sqrt{2z \sin \omega_1}}. \quad \dots \quad (24)$$

* Scientific Papers, vol. v. p. 620.

Since z is large the effective range of integration is large, but the terms αy^3 , βy^4 , only become appreciable compared with y^2 near the limits of integration. If we expand the cos term and omit the odd term containing the sines, as its integration from $-\infty$ to $+\infty$ is zero, we have

$$J_n(z) = \frac{1}{\pi} \sqrt{\frac{2}{z \sin \omega_1}} \int_{-y_1}^{y_1} dy \cos \{ \phi_1 - y^2 + \beta y^4 \} \cos \alpha y^3. \quad (25)$$

Approximate results are obtained by expanding $\cos \beta y^4$, $\sin \beta y^4$, $\cos \alpha y^3$ in series after expanding the $\cos \{ \phi_1 - y^2 + \beta y^4 \}$, and by making use of the integrals

$$\left. \begin{aligned} \int_{-\infty}^{+\infty} dy \cos y^2 &= \sqrt{\frac{\pi}{2}} = \int_{-\infty}^{+\infty} dy \sin y^2, \\ \int_{-\infty}^{+\infty} dy y^4 \cos y^2 &= -\frac{3 \cdot 1}{2 \cdot 2} \sqrt{\frac{\pi}{2}} = \int_{-\infty}^{+\infty} dy y^4 \sin y^2, \\ \int_{-\infty}^{+\infty} dy y^8 \cos y^2 &= \frac{7 \cdot 5 \cdot 3 \cdot 1}{2 \cdot 2 \cdot 2 \cdot 2} \sqrt{\frac{\pi}{2}} = \int_{-\infty}^{+\infty} dy y^8 \sin y^2. \end{aligned} \right\} \quad (26)$$

The result obtained in this way is

$$J_n(z) = \sqrt{\frac{2}{\pi z \sin \omega_1}} \left[\cos \left(\phi_1 - \frac{\pi}{4} \right) \left\{ 1 - \frac{7 \cdot 5 \cdot 3 \cdot 1}{2^4} \cdot \frac{\beta^2}{2} + \text{etc.} \right\} \right. \\ \left. + \sin \left(\phi_1 - \frac{\pi}{4} \right) \left\{ \frac{3 \cdot 1}{2^2} \beta - \text{etc.} \right\} \right]. \quad (27)$$

* These integrals are regarded as divergent integrals. By integrating by parts twice we readily obtain

$$\int_{-a}^{+a} y^4 \cos y^2 dy = a^3 \sin a^2 + \frac{3}{2} \cdot \frac{1}{2} \cdot 2a \sin a^2 - \frac{3}{2} \cdot \frac{1}{2} \cdot \int_{-a}^{+a} \cos y^2 dy.$$

Let a now become infinitely great. The integrated terms $a^3 \sin a^2$, and $a \sin a^2$, oscillate in value rapidly as a is increased, while the third term is a convergent integral. The results employed above are obtained by neglecting the oscillatory terms, and by taking the convergent integral to be the value to be assigned as a mean value of the required integral when a becomes infinite. The above cases are very similar to that of the Fourier integral in equation (1) of this paper: for a finite,

$$\int_0^a \cos kx dx = \frac{\sin ax}{x},$$

and when a is infinite, the integral has the value zero at all points except at $x=0$. The process of evaluation employed gives the correct values for the above integrals required in physical problems, and for integrals of the type contained in equation (1), several cases of which have been examined.

The expression given in (27) is in agreement with the well-known asymptotic expression except in the term containing β^3 . To bring the final term of (27) into complete agreement with the corresponding term of the asymptotic expression for $J_n(z)$, the auxiliary phase-curve must be modified by the addition of the term $\frac{z \sin \omega_1}{6!} \sigma^6$. When this term is included, we obtain by the above method an expression which is correct as far as the term containing $\frac{1}{z^{5/2}}$; and the higher terms are obtained correctly when a sufficient number of terms are employed in the auxiliary phase-curve.

Applications of the expressions contained in the present paper occur in the problem of determining the front of a group of waves advancing in shallow water, and in connexion with the minimum of the group-velocity in the case of waves governed by gravity and surface-tension combined. The theory also allows of an extension of the well-known solution of the ship-waves problem whereby the motion in the neighbourhood of the line of cusps can be determined with greater accuracy. There is also the question of energy propagation in wave-motion in the cases to which the theory given in the present paper is applicable. These problems are of interest in themselves and also on account of their bearing on analogous problems of wave-motion in dispersive media; they will be dealt with separately in later papers.

CXXII. *The Movements of the Earth's Surface Crust.*

By J. JOLY, *Sc.D., F.R.S., F.T.C.D.**

Introduction.

IT is well known that periodically the Ocean floods the lower land-surfaces of the earth, and that such transgressional seas prevail for so long a time that geosynclines receiving the sediments washed from some mountain range may accumulate debris to the depth of many miles.

But still more strikingly eloquent of vertical movements affecting the continents is the fact that the mountains themselves are mainly built of marine sediments, although batholiths and other igneous bodies exist within.

The mountains clearly reveal the effects both of horizontal and vertical movements in the form of folding, overthrusting, block-faulting, etc.

* Communicated by the Author.

Furthermore, it is known that great mountain ranges now existing on the Globe received a remarkable increase of elevation during comparatively recent times; that these events were (geologically speaking) of simultaneous occurrence over the earth; and that wide-spread flooding of the land areas, with marginal and central transgressional seas, heralded these movements.

Looking back into the past we find over and over again evidence of similar events and always in the following sequential order:—(a) Prolonged crustal disturbances leading to fluctuating transgressions; (b) Greater and more permanent transgressions and, often, much local accumulation of sediments; (c) Mountain elevation and retreat of the continental seas; (d) Final great elevation of the mountain ranges and restoration of former continental levels. Attending these movements of the earth's crust volcanoes may break out on a great scale and vast floods of lava may escape at low levels, especially along the western margins of the continents or to the west of high mountain ranges.

The events which heralded the great "revolution" of Laramide times in N. America, and their final consummation in the elevation of the Laramide ranges, may well illustrate this succession of crustal movements. And, again, very many millions of years earlier—in Permian times—similar phenomena affected the same continent when the Appalachian ranges originated. Earlier still, near the close of the Pre-Cambrian and, finally, away back in the Archæan, one or two revolutions of extreme intensity and very long duration appear to have affected, to the point of complete transformation, the entire land-surfaces of the Globe.

Between these events, which seem to be cyclical in recurrence, lesser disturbances affected the crust—disturbances eloquent of unstable conditions and of some source of restless energy existing beneath.

Now, in this present paper I venture on an endeavour to trace the origin and inter-relation of these various events to:—(1) The existence of a general basaltic magma-ocean or isostatic layer in which the continents float and upon which the oceans rest; (2) The presence of a certain amount of radioactive materials throughout this magma-ocean; (3) The maintenance, both in the past and in the present, of isostatic equilibrium of the land-masses; (4) Certain forces acting on the earth's surface materials, forces of astronomical origin: *i. e.* tidal and precessional.

We shall first consider the existence and nature of the magma-ocean.

Existence and Nature of the Magmatic Layer.

The evidence for the existence of such a layer extending beneath the continents and oceans primarily arises from the support which the theory of isostasy has received in recent years. No one who has followed the evidence can question the fact of continental flotation and of the existence of downward extending "compensations" buoying up the greater raised features of the earth. These facts involve a sustaining, sub-continental layer. That this layer must be composed of material denser than the average continental rocks is evident. We have further guidance as to its nature in the great outpourings of basaltic lava at intervals in the earth's history, dating back to most remote times; and, again, in the fact that by far the greater number of the volcanoes of the Globe emit basalt. Yet another fact points to this rock-substance as composing the magma-ocean—its relatively low melting-point. Plainly the sustaining ocean must be of lower melting-point than the average continental rocks. The melting-point of the latter varies from 1400°C. to 1700°C. ; the melting-point of basalt is below 1200°C. under like conditions of pressure.

The view that basalt composes the isostatic layer is supported by many petrologists. Notably, Daly ('Igneous Rocks and their Origin,' 1914), dealing with the problems of magmatic differentiation, volcanicity, etc., thus summarizes his conclusions:—"The facts of Volcanic Geology seem, therefore, to co-operate with the facts of plutonic geology in showing that the essential process in igneous actions on this planet is the rise of basaltic magma from the universal substratum along abyssal fissures" (p. 303).

The depth of the layer required by the theory of isostasy is not closely determinable. Some of the best authorities consider the most probable depth to lie between 60 and 70 miles.

Thus we perceive that basalt is the most prevalent and most important rock-material of the outer part of the Globe.

Melting of the Magma.

All basalts so far examined reveal small quantities of radioactive materials, both of the Uranium and Thorium families of elements. There are quantitative variations—relatively fairly considerable—but always actually concerned

Phil. Mag. S. 6. Vol. 45. No. 270. June 1923. 4 F

with minute amounts, as the following table will show * :—

	Ra. grm. per grm. $\times 10^{-12}$.	Thorium grm. per grm. $\times 10^{-5}$.
11 Basalts (chiefly Hebridean)	0.5	0.38
5 Gabbros and Norites	1.3	0.50
8 Diabases and Dolerites	1.0	0.22
14 Basalts and Melaphyres (chiefly Deccan and Antarctic)	2.0	0.84
18 Basalts (generally representative).....	1.4	0.63

It is well known that radioactive substances generate heat at a constant rate which no extremes of pressure or temperature hitherto tried affect or modify in the smallest degree. It may, therefore, be assumed with certainty that, *if the conditions prevailing in the magma are such that this heat is conserved, ultimate fusion of the whole mass is inevitable.* It must be kept in mind that this ceaseless generation of thermal energy progresses in every gram, in every cubic centimetre, throughout the whole body of the material.

The physical conditions otherwise affecting the magma are not everywhere the same; the pressure, of course, increases all the way down, and this will influence the melting-point, latent heat, and thermal expansion, as will be referred to again further on. When, therefore, we ask the question as to how far would attainment of the state of fluidity be a simultaneous phenomenon, we must answer with respect to the upper regions only; and always bear in mind that the word "simultaneous" is taken in its geological sense.

If we assume that at some stage in the history of the magma it is at its melting-point but in a state of quasi-solidity, lacking the latent heat necessary to produce liquefaction; then after a certain period the several constituent parts, differing in their radioactive content, melt in the order of their radioactivity, the richest melting first.

Now, in a region of the magma where the main body is still solid, nothing can come of such local fusion save that these more radioactive centres share their accumulated heat with surrounding basalts, causing them to melt and bringing about thereby intermingling with the poorer magma. Unless the heterogeneity of the magma with respect to radioactive constituents be on a very great scale (which we have no reason to believe is the case) this must be true.

* J. H. J. Poole, "The Average Thorium Content of the Earth's Crust," *Phil. Mag.* Apr. 1915; J. Joly, "The Radioactivity of Terrestrial Surface Materials," *Phil. Mag.* Oct. 1912.

This gradual, part-by-part, liquefaction of the magma must persist over a very long period. It represents the period of preparation for a great revolution. Volume changes (to be considered presently) are locally produced which may be of sufficient magnitude to affect restricted areas at the surface. The condition of change must continue until there is a final and general breakdown of the residual "rigid" ground-mass of the magma. When this occurs, and only then, the climax of a revolution is reached. Thereafter convective circulation on a big scale begins and the slow thermal flux permitted by the conductivity of the medium gives place to active circulation—melting and stoping of such surface-layers as may yet have escaped fusion and the convective distribution downwards of the cooled and denser magma which results.

We notice that in this sharing of heat among the constituent parts of the magma—the richer magmas melting down the poorer—it follows that neither the richest nor yet the poorest lavas determine the duration of the period required for the thermal accumulation to reach that critical amount which determines general fusion, but the average. A little consideration, in fact, shows that the extremes cannot control the date of the final breakdown.

Hence, in our time-estimates we take the mean values of the quantities of radium and thorium contained in the basalts (and their equivalents) as giving the best clue to the time-intervals which must separate world-wide revolution. For, as will be seen later, our assumption is that it is the volume-changes arising in the liquefaction of the abyssal magma which determine the most conspicuous events then taking place at the surface.

Now the radium content of a composite powder made up of 18 representative basalts*—as determined by the fusion method—and the thorium content as determined by the continuous-ebullition method (Phil. Mag. July 1911 and May 1919) are respectively—as cited above— 1.4×10^{-12} and 0.60×10^{-5} gram per gram. The heat continually evolved by one gram of radium in equilibrium with its related elements is 5.6×10^{-2} gram-calorie per second. The heat evolved by one gram of thorium and related elements is 6.6×10^{-9} calorie per second, as determined by Pegram and Webb (Phys. Rev. xxvii. 1908), which is somewhat lower than the calculated theoretical amount (Rutherford, 'Radio-active Substances and their Radiations,' p. 583 (1913)).

* These include 3 Hebridean, 4 Antarctic, 3 Deccan, and basalts from the Eifel, Saxony, Hessen, Siebengebirge, St. Helena, etc. .

From these data we find that 11.8×10^{-14} calorie is generated per second in a gram of the rock, or 3.71 calories in one million years. In 25 million years 92.75 calories accumulate in every gram. If we accept for the radium content of the average basalt 1.2×10^{-12} gram per gram, we find that it takes 28 million years to accumulate 92.4 cal. per gram. According to Vogt (*Christiania Vid. Selsk. Skrifter*, 1904, p. 54 *et seq.*), the latent heat of such rocks may be taken as 90 calories. So also the experiments of Hempel and Heraeus (*Zeit. f. Elektrochemie*, 1903, p. 43) give the latent heat of fusion of Melilite (a substance somewhat analogous to basalt in chemical composition) as 90 gram-calories. Doelter (*Phys. Chem. Mineralogie*, p. 101) states that the latent heats of fusion of silicates are mostly around 100 gram-calories per gram.

We conclude that the latent heat required to liquefy 1 gram of average basalt at its melting-point would take about 30 million years to accumulate.

Volume-Change of the Magma.

The effects of pressure in modifying this conclusion are not definitely known. The melting-point rises with pressure. Vogt (*loc. cit.* p. 210) concludes that the pressure due to 25 miles of rock would raise the melting-point 50° C. Tamman gives reasons for believing that the positive volume-change, $V_1 - V_2$, becomes negative under very high pressure and consequently from the thermodynamical relation between melting-point, pressure, and volume-change, the melting-point will reach a maximum with increase of pressure and will then fall. Such a pressure as would prevail at a depth of 150 kilometres would give rise to the maximum melting-point (Vogt, *loc. cit.* p. 208). On this basis the melting-point continues to rise all the way down to the base of the magma-layer if the layer be such as isostasy requires. The whole matter is complicated by the effects of occluded gaseous matter, which seems to reduce viscosity and to confer considerable expansive force under decreasing pressure, *i. e.* attending vertical circulation.

However, as will be seen later, when fusion at length occurs in the upper parts of the magma certain tidal disturbances must arise. Currents to feed the tidal wave must originate, and these must grow in importance as melting progresses and the tidal effects augment. Such disturbances must be transmitted downwards, and even the lowest layers may be affected. It seems, therefore, probable that, when

melting becomes general above, there must arise ascensional movements wherever the conditions of viscosity permit. As matter of observation, at a very little over the melting-point basalt is an extremely mobile fluid.

There is another probable effect that must be borne in mind—supplies of heat from yet deeper regions of the earth may affect the lower layers. This is, in fact, certain, unless the earth be, for some reason, radium-free below some 70 or 80 miles down—obviously a most improbable condition. This is an added reason for the view that, when tidal effects set in above, grave disturbances may be transmitted far down and may bring up super-heated magma possessing great expansive properties due to its temperature and to juvenile gases. Daly (*loc. cit.*), in connexion with magmatic stoping by abyssal injection, has discussed similar problems.

Effects of the Volume-Change.

Now, the effects of general expansion will be to enlarge by a little the earth's radius. Both continents and ocean-floor will be upraised together. But change of density in those layers of the magma principally buoying up the continents will give rise to another effect. For, whereas the oceans are not floating by displacement, the continents are. Thus a general increase in the volume of the magma will raise both together, but the attendant change of density will cause the continents to sink. The result of this effect at the surface will be transgression of the sea upon the land.

It is difficult to give numerical estimates of the magnitude of this effect. The experiments of Day, Sosman, and Hostetter (*Am. Journal of Science*, Jan. 1914) seem in many respects the best we have. The volume-change attending fusion is sudden and amounts to 10 per cent. of the volume of the unmelted solid at its melting-point—or 12 per cent. of the volume of the crystallized basalt at or near the melting-point. There is a sudden and marked liberation of heat attending the change to the solid crystalline state. This is a restoration of heat from the latent to the sensible state. Its amount was not measured.

We cannot apply these figures directly to estimates of continental sinking and oceanic transgression, for the reason that it is improbable that the whole continental compensation is affected by it. This much may, however, safely be affirmed:—*The observed volume-change of basalt in changing state appears to be fully adequate to account for the most extreme transgressions revealed in past geological records.*

Cooling of the Magma.

Now, it may take some 25 or 30 millions of years to effect such a storage of heat as will result in a general change of state.

When, finally, fluidity is attained convective circulation begins, and cooling will be rapid. But while such rapid cooling will progress beneath the ocean floor, there will be then and at all other times, relatively little cooling immediately beneath the land-masses. We may take this last point first.

The fact is easily demonstrated. From their proper radioactivity and probable thickness the continental masses must possess basal temperatures approximating to that of the underlying basalt. In other words, both now and at any other time the gradient of temperature prevailing in the earth's continental crust is mainly due to the generation of radioactive heat within its own materials, and not in any notable degree to heat flowing up from subcrustal sources.

For suppose the continents to average 24 kilometres (15 miles) in thickness. Throughout this depth we infer from measurements applied to representative rocks that there is 2.2×10^{-12} gram radium and 1.6×10^{-5} gram thorium in each gram of rock (Phil. Mag. Oct. 1912 and Apl. 1915). The thermal output from these quantities of radioactive elements is 22.8×10^{-14} cal. per second. On a specific gravity of 2.7 this works out as 1.5×10^{-6} cal. per second for a volume 1 square cm. in cross-section and 24 kilometres deep. But the heat escaping at the surface, as calculated from a gradient of 1°C. in 32 metres and a conductivity of 0.005, is 1.6×10^{-6} calorie per second.

Thus, practically all the heat escaping at the surface of the continents has been generated within the rocks of which it is composed, and therefore cannot come from beneath. It follows that the radioactive heat generated immediately beneath the continents is at the present time being conserved—the floating land-masses acting as an adiathermenous layer to the underlying magma at or near the melting-point of the basalt.

However, although this, very probably, involves the local persistence of molten basalt beneath the crust, there must be considerable lateral circulation when consolidation is in progress beneath the oceans. For the loss of volume attending cooling must draw on the sub-continental magma to a considerable extent. There is also movement due to tidal effects, as already pointed out. If these effects result in the upper

parts of the magma shifting with reference to the deeper layers (as will, later, be referred to), this must give rise to horizontal shearing at all levels, and in this way sub-continental cooling and solidification will be promoted. When solidification is attained these tidal movements probably cease, or almost cease.

But the conditions of heat storage and heat loss beneath the oceans are in many respects different. There appear to be reasons for believing that not only will the conditions there prevailing lead to effective conservation of most of the energy during times of thermal accumulation, but also will favour its more rapid escape in times of revolution.

There is high probability, almost certainty, that the ocean floor is itself composed of basalt. The reason for this view is the fact that gravity measurements appear to show that the lesser density of the ocean is compensated by excess of mass beneath. In fact, the view has been advanced that the oceans are where they are because of this excess of mass. Again, the oceanic islands and volcanoes are strikingly basaltic in character.

But if composed of basalt then is the ocean floor exposed to fusion and stoping by rising currents of molten magma. The amount by which its thickness is reduced while it is borne upwards on the molten and expanding magma we do not know. But it is possible to arrive at some idea of what the initial thickness of the ocean floor may be before it is attacked by the liquefied lava beneath. By the "floor" is meant that topmost layer of the basaltic magma which falls in temperature below the melting-point.

The problem is similar to that solved by Lord Kelvin with respect to the downward distribution of temperature in a globe cooling from fusion by the passage outward of heat to an environment maintained at a constant low temperature. Kelvin's value for the diffusivity is inapplicable to the present problem, for it is, in fact, based on a mean experimental value obtained on substances only one of which (that on "the trap rock of Carlton Hill") is applicable to the present case. Correcting for this we next assume that the magma is everywhere solid in the sense that it loses heat by conductivity only, but is near its melting-point. The surface is maintained at 0°C . by the waters of the ocean. If, now 25×10^6 years are available for the growth of the sub-oceanic floor, we seek to find the distribution of temperature at the expiry of that period and the thickness of the floor—that is, the distance from the surface at which the temperature approximates to 1150°C . We find that

at 32 kilometres (20 miles), the temperature is nearly 1100°C .

In reaching this result we have, for purposes of simplification, neglected (a) the development of radioactive heat within the cooling layer; (b) the increased value of the thermal capacity of the basalt at high temperatures. According to Roberts-Austin and Rucker, Barus, and others (Vogt, *loc. cit.* p. 40) this varies from 0.180 at 20° to 0.285 at 1100° ; (c) change in the conductivity at high temperatures. H. Poole has found no variation up to 600° (Phil. Mag. Jan. 1914); but it is probable that at higher temperatures it will diminish. The effects of these variations will be to sharpen the gradient, decreasing the thickness of the layer. (b) must reduce it by some 15 to 20 per cent. and (a) at least as much again. The probable value would be about 15 miles.

This result—which, for want of the sufficient data, is an approximation only and may be excessive by 3 or 4 miles—enables us to conclude that during the inter-revolutionary period the cooling by conductivity will give rise to a gradient of temperature downwards, rising to the magmatic temperature at a depth of about 15 miles. This is the probable thickness of the ocean floor.

[It supports the view that below a certain depth, comparable with the thickness of the continental crust, there is complete conservation of radioactive heat throughout the period separating the great revolutions.]

These considerations give some clue to the conditions which may control the upward passage and escape of heat through the ocean floor, as estimated above, when the conserved heat beneath has accumulated to the point of bringing in a period of revolution.

It is evident that, when the magma beneath the ocean floor has become fluid and circulatory movements begin, the floor which covers in the magma is, at its base, at the temperature of the magma, and in its lower parts only requires the necessary latent heat to again revert to the fluid state. It will be, therefore, rapidly melted away. Neglecting the possible intensification of these effects arising from superheated lava rising from beneath, and assuming the entire layer to possess the melting-point of the upper stratum of lava, there must be rapid (geologically speaking) thinning of the sub-oceanic floor. It is quite possible that this thins out to an extent enabling the greater part of the stored latent heat to escape in a very few million years and before the floor is completely removed. Much heat will doubtless be lost by

igneous eruptions through the floor. But, again, neglecting such aid, it is easy to show that an ocean floor reduced to some two or three miles in thickness would permit of such a heat loss as would confer the quasi-rigidity and the density of the solid state upon the greater part of the magma, not only beneath the oceans, but beneath the continents.

An extreme case is to assume that *all* the latent heat of the entire magma has to escape through the ocean floor. Even were this the case, a floor 2 miles thick, possessing the conductivity 4×10^{-3} , would pass out all this heat in 8 million years, and, of course, one-half of this thickness would dispose of it in 4 million years. In point of fact, the escape in this manner of *all* latent heat would be impossible; because the circulation must cease when a certain fraction has become solid—sufficient to diminish tidal activity and to check convective movements.

Effects of the Cooling of the Magma.

We may now return to a consideration of the surface-effects referable to the changes progressing in the magma.

We saw that melting of the magma produced continental sinking and transgression of the sea upon the land. This we now refer to the conservation of radioactive heat within the magma under the conditions we have described. But we have also traced a source of rapid loss of heat and re-solidification of the magma. The surface-effects of this must evidently be the restoration of former continental levels with reference to the oceans. For, while both continents and oceans will be affected by the change in such a way as to move downwards, the buoyant effect on the continents must be such that these must rise relatively to the sea-level. Hence, transgressional seas will disappear off the land-areas.

The upward movement will more especially prevail where deep compensations exist. Such an up-lift as the worn-down Appalachians experienced in late Cretaceous times, or the vertical movements which affected the Andes in more recent times, doubtless originated in this manner. Mountain-building movements are, probably, largely referable to this density-change which sets in towards the close of a great revolution, as will presently be more fully explained.

The Time required for a Revolution.

It will be gathered from what has now been said that to the isostatic layer and its thermal fluctuations (arising cyclically from storage of radioactive heat to the point of

liquefaction of the layer), on the present theory, the vertical movements of the land are to be referred. And we have seen that the time intervals which, on our rough computation, we have arrived at are not inconsistent with estimates of geological time.

It would seem that four or five periods of major revolution can be recognized since Algonkian times, although geologists do not seem to be in perfect agreement as to the number of revolutions which are to be regarded as of world-wide significance.

It is inferred by many that the Palæozoic was preceded by such an event. Some American geologists call this the Grand Cañon Revolution. A second revolution is recorded in the Silurian and Devonian rocks :—the Caledonian Revolution. A third occurred in Permian times, known as the Appalachian. A fourth culminated late in the Cretaceous and early Tertiary, which was responsible for the major development of the Cordilleras of N. and S. America and in America known as the Laramide Revolution. A fifth ushered in our own times and is responsible for the principal development of the great Eurasian chains. It is known as the Alpine Revolution.

Now, these developments involve four periods of genesis comprised within what is called "The age of the earth." They are, therefore, on the lower estimates of this interval comprised within some 170 to 200 millions of years at most. The preparation for the Pre-Cambrian revolution probably extended back into more remote times. Thus some 40 or possibly 50 millions of years are required for the preparation, development, climax, and decadence of a great revolution. According to the view of some, far longer periods would be involved.

The Lateral Movements.

But the phenomena attending vertical movements of the land relative to the ocean are not the only cyclical events in geological history which call for explanation. For, as we have seen, attending these vertical movements we find evidence of lateral thrusting in the folding and horizontal dislocation of the rocks. The sources of vertical movements and of horizontal compression are, plainly, genetically connected. Of this there is no doubt, for all over the world the order and inter-relation of the events seems to have been the same; the greatest display of orogenic activity appearing towards the close of a great revolution and after transgressional seas have largely disappeared.

Now, there two sources to which lateral movements may be referred and which arise out of the physical changes experienced by the isostatic layer. Both these sources appear to be, in some degree, inevitable, and therefore are *veræ cause*, so that we conclude that both must have operated.

Mountain-building.

But before considering them it seems desirable to discuss for a little what the structural features of mountains actually reveal. Vertical movements are certainly demonstrated and often on a very great scale. The interest of the matter arises in the part played by horizontal movements. One eminent authority on isostasy—W. Bowie—considers that much of the rupture and distortion of strata, ascribed formerly to regional forces acting horizontally, are accounted for by vertical movements (“The Earth’s Crust and Isostasy,” ‘The Geographical Review,’ Oct. 1922). Horizontal movements have certainly contributed to mountain structure. Whether they play any direct part in the elevation of the mountain is another matter.

Going back to the loaded geosyncline, it is certain that this is a region of diminished rigidity within the continental crust. For the depression determined by isostasy exposes it to higher temperatures than prevail in the normal crust. The phenomena of regional metamorphism testify to the intensity of thermal conditions. Fusion may not be brought about (the melting-point of the floating continental crust is, as we have seen, from 200° to 500° higher than the m.p. of basalt), but rigidity may be so far diminished that comparatively small forces may give rise to the folding of strata.

Beyond the production of this lateral folding, there may be little more ascribable to horizontal forces. For, in fact, if the conditions of isostatic adjustment prevail throughout the genesis, vertical movements must be almost entirely due to buoyancy forces arising in the changing density of the magma.

We have to remember that, while the horizontal forces are in operation, the magma beneath is at its lowest density. At that period there is, in fact, very little difference in specific gravity between the continental materials and the melted substratum. It is therefore impossible that in this stage lofty vertical elevation could be attained. The compressed strata must go down and not up, and their downward displacement involves very little expenditure of energy. The

rise above the continental surface will be insignificant. The conception, therefore, that chains such as the Alps and Andes were forced upwards by lateral forces cannot be correct. The upward movements, according to the present theory, came later, when the heat-loss restored the higher magmatic density. Then the energy of upheaval is referable simply to the gravitational potential of a general raised magmatic surface over the earth. This falls a little when the mountain ascends. The effect is purely hydrostatic.

The Geologist is not, therefore, required to adduce horizontal forces of great intensity, but he must account for movements adequate to shorten, perhaps by a score of miles, the width of a sedimentary area. If the over-thrusting in the Alps has been correctly estimated, movements of twice or three times this magnitude call for explanation.

Lateral Forces arising from Change of Area of Ocean Floor.

We now return to the sources of mountain-building forces which arise from the changing physical state of the magma. Looking back to earlier stages of our argument, we find that the liquefaction of the isostatic layer involves an increase of the earth's mean radius. Taking the depth of the magma to be 70 miles and that at the height of a revolution it experiences an average volume-expansion of 10 per cent., we arrive at the following figures. The primary mean radius of the Earth is 3963.2 miles (its present value). This corresponds to an area of 197,380,000 square miles. The volume of the magma is obtained from this after deducting the displacement of the continents. Taking the area of the continents as 52.5×10^6 sq. miles and their immersion as 15 miles, the magma-volume comes out as 13×10^9 cubic miles. The increase of 10 per cent. is therefore 1.3×10^9 cubic miles, and the corresponding increase of the earth's radius turns out to be 6.5 miles—which involves an aerial increase of 650,000 square miles.

Now, this increase must fall upon the oceanic areas, because the continents are homogeneous and, in fact, are floating upon the expanding magma. The ocean floor is at this period being reduced greatly in thickness, due to the hot circulating lava. It must now break up under the expansive forces. It is rent by cracks, which again are filled in by abyssal injection, and before any considerable cooling has come about we must suppose that a larger ocean by some 650,000 square miles has come into existence, floored by a corresponding basaltic floor of a thickness which may be from 5 to 10 miles; possibly more; possibly less.

The increased surface-area of the earth arrived at above corresponds to a circumferential increase of 41 miles. This, also, necessarily falling upon the oceans means that the equatorial span of the Pacific will increase by 30 miles, and that of the Atlantic by 11 miles.

Attending the surface-solidification of the magma, the downward movement of the ocean floor gradually begins and the continents become pressed-upon, on every side, by the enlarged and strengthened oceanic floors. Even if buckling of the floor results the lateral pressure must continue, for the rigidity of the cooled basalt is considerable. This effect will give rise, pre-eminently, to very intense horizontal thrusts (although of limited range) on the continental land-masses. The pressure must long continue and may be adequate to find out the weak places of the land and to fold and shear the sediments in the upper few miles of the geosynclinal accumulations, seconding the intervention of other forces to be presently discussed.

As regards the estimated magnitude of this expansional effect, the amount of the volumnar expansion assumed is, to some extent, arbitrary. The upper part of the magma may, indeed, enlarge or contract by some 10 per cent. of its volume in changing from solid to liquid and *vice versa*. The volumnar change of the deeper parts is unknown, but if—as appears probable—there is vertical circulation of super-heated material, the volume-change may be considerable. The assumption of a mean change of 10 per cent. may, however, be somewhat excessive.

It is noteworthy that the amount of attendant change in the magnitude of the ocean floor is in no degree affected by thermal expansion or contraction of the floor itself. For, in point of fact, the mean temperature of this crust is unchangeable, its upper and lower surfaces maintaining unchanging temperatures—*i. e.* controlled above by the ocean of water and beneath by the melting-point of the ocean of basalt.

Upon the question as to the adequacy of such movements as might arise from this source, it is to be observed that they are repetitional with each revolution. Thus the total horizontal contraction involved in the Rocky Mountains has been estimated at 25 miles east to west. But this range was mainly created in Laramide times. It was again further acted upon in Pliocene times. The latter disturbances chiefly took the form of vertical uplift. But, as we have seen, there is no vertical uplift without previous downward displacement into the isostatic layer. The downward displacement may be due to geosynclinal loading alone or to-

loading subsequently disturbed by lateral forces. It seems, therefore, probable that lateral forces, acting during two successive revolutions, were responsible for the Rocky Mountains as we see them.

Accompanying the volume-changes of the isostatic layer there would arise a small effect upon the rotational velocity of the Earth. The retardation attending expansion of the magma and increase of the Earth's radius would be temporary, however—the original velocity being restored upon the shrinkage of the magma. It does not appear that this temporary effect would in any appreciable degree affect the changes we have been discussing.

The Inter-revolutionary Disturbances of the Crust.

But, in addition to the major movements attending world-wide revolutions, there are minor ones—often not inconsiderable, however,—which appear to occur at irregular intervals and which involve not only a certain amount of transgressional flooding but also orogenic movements in a horizontal direction.

I think we may refer these disturbances largely to conditions similar to those we have been considering. For, while we have dwelt upon the broad features of magmatic changes over geological time, it is impossible to maintain that more local thermal fluctuations at irregular times have not occurred (*ante*, p. 1171). The floating land must, in fact, be continually subjected to the effects of changing buoyancy. This was especially noteworthy in the geological history of the Pacific borderlands of North America. Transgressions and re-elevations were frequent events. But the forces of uplift must have affected the adjacent ocean floor for many miles to the west, and the fractures induced by tensile stresses must always be repaired by abyssal injections. There is no other way. Attending downward movements, compressive forces must accordingly arise along the continental margin. This seems quite inevitable. The only question at issue is really one of the adequacy of such repetitional movements. This question we cannot answer. But such as they were these forces were many times repeated. Schuchert ('Text-book of Geology,' p. 979) estimates at least eight minor periods of crustal disturbance as having affected the continent of North America. Again, we must recognize the fact that local vertical movements of an oscillatory character affecting a continental interior cannot take place without engendering horizontal compressional

movements on the same mechanism as I have referred to above. In short, from the physical properties of rock towards tensile and compressive forces, and the ever-present existence of the abyssal magma beneath, ready to enlarge such cracks as may develop and infill them with rock-making materials, pulsatory vertical movements may account for much crustal distortion. Horizontal forces directed in any azimuth may be engendered in this way.

In the case of the greater world-wide movements when the rise and fall of the entire crust takes place the wider the oceanic reach the greater must be the orogenic effects. Here we recall the significant remark that the greatest mountain ranges face the widest oceans. There are no mountains around the Atlantic comparable with the Cordilleras. The Himalayan fold-mountains range perpendicularly to one of the greatest oceanic reaches of the Globe.

Effects of Tidal and Precessional Forces.

But other factors arising from the existence of a radioactive isostatic layer may enter into this question, and possibly upon a very effective scale. I mean precessional and tidal forces.

It is recognized in tidal theory that the tidal wave which is maintained on opposite faces of the Globe must act as a brake applied to the surface of the earth opposing its axial rotation. This brake, operating to retard the west-to-east motion of the earth's surface, may be expected to give rise to a motion of the whole outer crust of the earth with reference to the interior—that is, if viscous movement of the outer over the inner parts is possible. In this way the length of the day may not represent the real rate of rotation of the earth, which spins within the outer crust with slightly greater angular velocity. Darwin ('The Tides,' p. 276) looked to such effects acting, in earlier periods of the World's history, upon a viscous planet as possibly wrinkling the surface in such a manner as to mould the observed continental contours. Eddington ('Nature,' Jan. 6, 1923) considers it possible that purely oceanic tidal movements, brought to rest in land-locked areas, might have given rise to crust-wrinkling.

The tide generating force is intrinsically a feeble force at the present time. The horizontal tidal force is only one eleven-millionth part of the weight. In past times, according to the tidal theory of the Moon's history, the force

must have been far greater, the horizontal tidal force increasing inversely as the 6th power of the Moon's orbital radius.

According to the theory I have been discussing, at intervals in the world's past history there came into existence a sea of molten rock having a depth probably not less than twenty times that of the ocean and possessing three times the density of water. In its upper parts this lava-ocean was, probably, highly mobile—quite as mobile as water. My own observations (Trans. R. D. S. vi. p. 283), made some years ago, showed that basalt raised just above the full melting-point possesses much the same properties as a very "thin" oily fluid. Day and his colleagues (*loc. cit.*) record similar observations. The question arises, how far may tidal movements prevailing in such an ocean have contributed towards crustal disturbances in the past and how much would they be effective even in Pliocene times or in the future? Data as to the downward viscosity of the magma-ocean are not available, and doubtless they must be important factors in determining the answer to these questions.

But it seems allowable to infer that the effects of world-revolutions must have been to develop retardative forces acting on the outer crust of the earth much in excess of anything of the same kind due to the oceanic tides of our time.

Now, if any considerable retardative effects affected the surface-features of the earth—I mean the continents and oceans and the ocean floor—so as to withhold them from partaking of the full west-to-east angular velocity of the earth, this effect of tidal force would seem to involve local stresses on the more deeply immersed parts of the floating land-masses, which might be very considerable.

To understand this we must note that the retardative effect referred to must be effective chiefly in the upper regions of the magma ocean, for its lower layers, in contact with more rigid materials beneath and, owing to pressure, probably possessed of greater viscosity than the upper layers, must partake more nearly of the full angular velocity of the earth's rotation. It is easy to see that these conditions must give rise to a west-to-east drive or pressure of the heavy magma against the immersed parts of the continents. It must be remembered that this state arises at a time when the ocean floor has been reduced in thickness, so that the submerged western coasts of the continents are left exposed to the effects of differential movements in the magma. For, in fact, the horizontal tidal forces exert an east-to-west pull upon the continents, and this is resisted by the earth's

rotational energy transmitted through the medium of the molten magma.

These conditions involve differential effects upon the floating land-masses. For the more deeply compensated continental features experience the west-to-east magmatic drive more than shallower land-masses. And, again, turning or rotational forces would arise, due to those greater downward extending compensations which might be located excentrically respecting the resultant or centre of magmatic forces, or where continental masses extended partly into equatorial areas—the linear velocity of the magma being greatest at the equator. Such rotational effects may have affected mountain development. Comparatively small movements would suffice: thus, if the African continent and Peninsular India were, even to a small extent, affected in this way, by the more active equatorial currents upon their southern extension, much of the Eurasian folding would find explanation. We have seen that at the height of revolution the ocean floor is, probably, much disturbed as well as reduced in thickness, and its resistance thereby diminished.

The effects of these conditions on mountain-folding would, probably, be principally experienced where the geosynclines had forced the land deep into the magma. Here the east-going magmatic pressure would be largely concentrated and the temperature conditions also most severe; lateral folding and compression into still greater depths—the conditions being self-intensifying—being a very probable result. Even under pressures of no very great intensity per unit area, provided they were long continued, these results might be expected. The final buoyancy effect would ultimately force upwards, isostatically, the bent and folded masses—along with batholithic invasions of the basaltic magma. Thus the ranges raised above the general continental levels would be formed.

The Cordilleras of western America would seem to stand as a monument of the forces acting from west-to-east which we have been discussing. It may well be that, whereas both the west and east coasts of the Pacific owe to an expanded ocean floor the major wrinkling of the continental surface, the predominant orogenic phenomena displayed on the eastern coasts is due to a force which cannot have acted upon the western coasts—the magmatic pressure arising in horizontal tidal and precessional forces.

Schweydar (*Zeitschr. d. Ges. f. Erdk. zu Berlin*, 1921, S. 120–125) has investigated a precessional force, which tends to urge the continents westward, and which has, of course,

Phil. Mag. S. 6. Vol. 45. No. 270. June 1923. 4 G

like the tides, an astronomical origin. From his statement it appears that this force must be considerably greater than the horizontal tidal force, and, obviously, its effects must greatly augment in times of revolution. It is strongest at the equator and is null at 36° N. and S. It must conspire with the tidal force to retard the west-to-east movement of the earth's crust. (See also Wegner, *Die Entstehung der Kontinente und Ozeane*, Berlin, 1922.)

It is significant as regards this probable intervention of tidal and precessional effects that the great lava-floods of geological history have welled up through fissures on the western sides of continental land or west of great mountain ranges, or, again, have appeared where rifts ranging north and south have been attended by deep crustal faulting and sinking. The Deccan basalt thickens towards the west, and western coastal fissures have been traced. The Hebridean basalt was poured out westward of a continent. The Disco basaltic flows appeared to west of the Greenland ranges. The western inter-montane regions of North America are largely flooded by basaltic outflows. The great African rift appears to have determined intense volcanism and basaltic outflows. The Christiana rift seems to be a similar case. The existence in revolutionary times of easterly basaltic pressure beneath would account for this remarkable localization of igneous activity.

Volcanic Activity and the Present Theory.

The present theory involves a probable decadence of volcanic activity in inter-revolutionary times. The existing explosive type of volcanism is, doubtless, a purely local phenomenon in many cases, the supply of thermal energy coming from deep-seated pockets of the molten rock. But volcanic activity may be associated with seismic indications of tectonic features, which seem to refer it to the activity of the general fluid substratum beneath the continents; or of sub-oceanic supplies which at the present time lie beneath an ocean floor which is still undeveloped. Cases of volcanism of this type, of a remarkable character, are reported from Japan and elsewhere. The great lava-flows are, however, a feature of revolutionary conditions, which must on a great scale cease with the cessation of tidal movements. Still, phenomena of the sort might long survive, for sub-crustal reservoirs of the molten magma, if once enclosed by solid rock, would cool with secular slowness; and any source of compression—such

as shrinkage of the containing rock or earth-movements—might bring it to the surface. The Icelandic eruptions of recent times may originate in this manner.

The higher volcanic cones do not appear to emit lava. Light ejectamenta—dust and steam—may be emitted. It is doubtful if, at their existing elevation, any definite lava-flows have taken place. Bonney ('Volcanoes,' p. 275) refers to this as a general feature of volcanism. The volcano outgrows its strength. The comparatively recent final elevation of the Andes may have operated in this way.

However, on the theory herein advocated, the lava-supply of volcanoes does not call for hydrostatic pressures extending into the depths. It is more probable that the lava-supply arises in laccoliths and such-like bodies which have been carried up with the general mountain elevation, and which for long ages are adequate to supply the comparatively small trickle which constitutes a volcanic eruption. As regards the fact that volcanoes emit magmas of various rock-clans, Daly has treated the matter so clearly and ably that it suffices to refer to 'Igneous Rocks and their Origin.' As stated above, there is no reason to suppose more than the one abyssal magma of basaltic composition.

Broadly viewed, volcanic and seismic phenomena are surviving memorials of past times, when the continents were exposed to vertical and lateral disturbances far greater than prevail to-day. The stored energy must be very great when integrated over large areas. It exists partly as uncompensated gravitational potential; partly as elastic potential, which can run down only by effecting structural readjustments. It is doled out age after age in the form of slow elevations and depressions, crumpling and faulting, in seismic and volcanic effects which in themselves are relatively local and petty phenomena. Denudation very often pulls the trigger in these cases.

The Dominance of Radioactivity.

Throughout the whole great matter we recognize in radioactivity a source of energy which has controlled the surface-history of the Globe. In the fusion and expansion of the isostatic layer the vertical movements are directly involved. When the mountains finally arise under isostatic forces the general magmatic level sinks a very little. Local movements of radioactive heat may control inter-revolutionary disturbance. Changes in the sub-oceanic floor may give

rise to lateral pressures. Again, radioactive heat prepares the way for tidal or precessional forces to intervene, and the surface of the earth becomes for the time being a brake applied to the rotating planet—a brake which absorbs some of the energy of rotation and for long ages afterwards exhibits the diastrophic effects.

The Question of Continental Drift.

The question of the possibility of continental movements having occurred in past times arises naturally in connexion with the foregoing views. The main point at issue, however, is one which we do not seem able to determine—how far, during times of revolution, the ocean floor may have been reduced in rigidity and thickness. For it is obviously hard to imagine that in times when a thick and rigid ocean floor binds the continents together—any forces with which we are acquainted can have attained such intensity as to rupture the connecting crust. However, during the height of a great revolution, under the operation of convective currents—probably in part superheated—assailing the basaltic ocean floor, almost anything may have happened so far as the stability of the floor is concerned. It may have been fractured or softened to an extent permitting of differential forces—already referred to as arising from tidal or precessional sources—to occasion slow drifting from west-to-east. For such must be the direction of continental movement relatively to the earth's surface.

Under such conditions Eurasia may have drifted from America in Laramide times. New Zealand, in virtue of its great loading of mountain ranges, may have parted from Australia; the Festoon Islands may have been carried eastward from Asia; Peninsular India may have parted from the African Continent; etc., etc.

But, as I have intended to convey, while the possibility of continental drift appears to be involved potentially in the present views, the former existence of all the necessary conditions does not seem to be demonstrable. Final support to the theory of continental drift must come from evidence which it is outside the scope of this paper to discuss.

CXXIII. *Notices respecting New Books.*

An Introduction to the Chemistry of Plant Products. Volume 2. *Metabolic Processes.* By P. HAAS and T. G. HILL. London: Longmans, Green & Co. Price 7s. 6d.

THE present volume forms a sequel to the volume by the same writers 'On the Nature and Significance of the Commoner Organic Compounds of Plants,' which was recently published. The volume treats a series of the more important outstanding problems of the synthesis or the building-up by the plant of fats, carbohydrates and proteins, of respiration—the production of energy for the maintenance of the life of the plant, and growth—the balance between these constructive and destructive processes.

The authors have courageously put aside the task of giving a mere digest of the literature of the problems with which they deal, and the book is consequently more likely to inspire students ultimately to turn their attention to serious problems needing original treatment than the usual text-books. Their self-imposed task has been to describe the present position in the various problems under consideration, in order to make as plain as possible the outstanding difficulties, as well as to explain the methods by which the results already reached have been obtained.

In the section dealing with the problem of growth the pre-occupation of the authors with the so-called "Compound Interest Law" is to be regretted. The exponential and logarithmic laws are but isolated examples of mathematical functions, and the prior probability of the growth-curves conforming to these laws is by no means large. Strong evidence of growth-curves agreeing with these curves is necessary before a reasonable probability for this hypothesis of growth can be established. A more illuminating treatment of this important and fundamental problem seems to require a freer use of mathematical functions. No structural problem in any branch of mathematical physics of the same order of importance has ever yet been solved by complete adherence to one type of solution, without reference to the general characters of the phenomena under discussion.

The experimental side of the problems under consideration is, on the whole, left on one side. It was plainly not necessary or desirable to burden the book with detailed discussion of points of purely experimental interest.

The Mathematical Theory of Relativity. By A. S. EDDINGTON. Cambridge University Press. 20s. net.

THE first draft of this book has been accessible for some little time in the form of a mathematical supplement to the French edition of the author's 'Space, Time and Gravitation.' This draft has now been developed into a more systematic and comprehensive treatise on the mathematical theory of relativity.

The author is concerned to work out deductively the whole theory from the premisses suggested by Einstein, and there is consequently no attempt at explaining in general terms the revolution of thought which the theories of relativity have initiated. With this subject matter the book must necessarily be mainly an exercise in mathematical deductions from highly abstract premisses.

The first section of the book gives a quasi-mathematical, quasi-philosophical introduction to the subject. It is much condensed, and needs to be read in connexion with the author's previous work, in which the point of view of this introduction is worked out *in extenso*.

The major part of the book deals with the theory of Tensors. It will be of great value to have in the present very clear and easily accessible form the body of tensor analysis as it is required for the development of relativity theory. The author's own generalization of Weyl is also included. Time alone will show how far this or any other attempt to link up relativity ideas with atomic structure and the Quantum theory will be successful.

Principles of Geometry. By H. F. BAKER, Sc.D., F.R.S., Lowndean Professor of Astronomy and Geometry, and Fellow of St. John's College, in the University of Cambridge. Volume II. Plane Geometry, Conics, Circles, Non-Euclidean Geometry. Cambridge University Press: 1922. Price 15s. net.

PROFESSOR BAKER gives plenty of good material in his second volume, but he makes it a little difficult to assimilate by not laying sufficient emphasis on the structure of his subject. His intention to be practical is perhaps carried out at the expense of obscuring to a certain extent the principles which it is his main object to expose.

As far as the experienced reader is concerned, this does not matter very much, as it is a comparatively simple matter for him to disentangle the principles from the details, which, indeed, illustrate the principles admirably. But it undoubtedly makes the book very difficult for one who is not in such a fortunate position.

The "symbols" which play such an important part in the book call for rather more explanation than appears to be given. They cannot be symbols in the ordinary sense because they are themselves symbolized; they are plainly logical constructs of some kind or other, and ought to be explained.

A great many readers will undoubtedly feel very grateful to Professor Baker for the way in which he has carried out the arduous task of expounding the principles of Geometry. The principles of Analysis are simple enough, for there is only one kind of analysis. But those of Geometry are another matter. There are many kinds of Geometry.

Synthetic Colouring Matters: Vat Colours. By Prof. J. F. THORPE, F.R.S., and C. K. INGOLD, D.Sc. Monographs on Industrial Chemistry. Edited by Sir EDWARD THORPE. Pp. xv+491. London: Longmans, Green & Co. 1923. Price 16s.

THE discovery of the constitution of Indigo led to the synthesis of a number of analogous coloured bodies, all of which like Indigo are insoluble in water; in order to employ these substances as dyes they have first of all to be converted into the colourless water-soluble leuco-compounds, which by subsequent oxidation produce the insoluble dye upon the fibre. This process, known in technical practice as vat dyeing, is essentially the same as has been practised by primitive races from time immemorial with Indigo. Since the commencement of the present century a large number of anthraquinone derivatives with similar tinctorial properties have been put upon the market, and the wide range of colour and fastness of these substances makes the vat dyes amongst the most valuable of all colouring matters. The present volume contains an account of the chemistry of these very numerous and intricate substances, the complexity of which is shown by a glance at their structural formulæ, which are given with lavish profusion throughout the book, and the specialist requiring information concerning the preparation of any particular member of the group will find a mass of information collected together within its pages. To the general reader, however, the first three chapters will especially appeal, since they contain an interesting historical survey of the subject of dyeing including such questions as the woad staining practised by the Ancient Britons and mentioned by Cæsar, and also the nature and origin of the Tyrian purple of the ancients.

It is to be regretted that the publishers have seen fit to have the book printed in Germany, but the cost of putting up the structural formulæ may well have been prohibitive in this country.

CXXIV. *Intelligence and Miscellaneous Articles.*

ELECTRIC FIELDS DUE TO THE MOTION OF CONSTANT ELECTROMAGNETIC SYSTEMS.

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN a footnote on page 1124 of the *Philosophical Magazine* for December 1922, Dr. S. J. Barnett, in referring to my paper "Unipolar Induction" (*Physical Review*, vol. xv. pp. 365-398, 1920), makes the following statement:—

"In connection with this experiment Swann, *l. c. ante*, has stated that Maxwell's equation (1) cannot be applied to the case

of rectilinear motion to show that the field is polar *because* (he states) *in this case the vector potential is not independent of the time*. This is clearly an error. Several examples of the contrary are given above, in addition to this particular case."

It is perhaps hardly necessary to do more than quote the statement in my paper to which Dr. Barnett refers to show that he has inadvertently misquoted me. The statement in question occurs on page 390 of my paper, and is as follows:—

"We cannot immediately import the ideas we have invoked in the case of uniform rotation to explain a shielding effect of the type referred to, because the vector potential is not independent of the time in the case of rectilinear motion; so that it is not immediately obvious that the whole of the field E as given by (5) is derivable from an electrostatic potential."

I think that this statement can hardly be taken to imply that equation (5), which is Dr. Barnett's equation (1), cannot be used for the proof of the result in question, for the case under discussion, but only that the result does not follow *immediately* as it does for the case of rotation. In fact, it is implicitly on the basis of equation (5) that I prove the result in my paper; and every expression for E in that paper is obtained directly or indirectly from this equation, whose truth is universal.

In so far as Dr. Barnett makes reference to other theorems, points of view, and discussions in my paper, I may say that it was not my intention to claim that these were entirely new, even though some of them might not have been published before. Indeed, I have always maintained that, from the standpoint of one who accepts the classical electrodynamics, none of the usual experiments concerned with moving lines of magnetic force present the slightest difficulty. It is only in extending the moving-line theory to forms inconsistent with classical electrodynamics that difficulty is encountered. To discard the conception of moving lines entirely would be unwise, since it certainly gives correct results in the most important cases, so one of the main objects of my paper was to formulate the exact sense in which the moving-line theory must be used if it is to lead to results consistent with classical electrodynamics. A sufficiently large number of experiments claiming to demonstrate difficulties in electromagnetic theory, and involving arguments concerning moving lines of force have appeared, even within recent years, to warrant such an attempt to crystallize the situation.

Yours faithfully,
W. F. G. SWANN.

Department of Physics,
University of Minnesota, U.S.A.
March 8th, 1923.

INDEX to VOL. XLV.

- ADCOCK** (F.) on temperature measurement with the Einthoven galvanometer, 532.
- Addenbrooke** (G. L.) on the electrical properties of a flint glass of density 6.01, 516.
- Adeney** (Prof. W. E.) on the aeration of quiescent columns of distilled water and of solutions of sodium chloride, 835.
- Adsorption from the gas phase at a liquid-gas interface**, on, 1088.
- Aeration of water and solutions of sodium chloride**, on the, 835.
- Alpha-particles from polonium**, on the range of the, 379.
- Aluminium**, on the mass-spectrum of, 942.
- Amalgams**, on the spectra of, 181.
- Antimony**, on the mass-spectrum of, 943.
- Apparatus for observing the rate of reaction between gases and liquids**, on an, 581.
- Appleton** (Dr. E. V.) on the representative differential equation of the triode oscillator, 401; on ionic oscillations in the striated glow discharge, 879.
- Arc**, on the mechanism of the electric, 1139.
- Argon**, on the ionization by collision of, 353; on the radiation and ionization potentials of, 480.
- Aston** (Dr. W. F.) on the mass-spectra of chemical elements, 934.
- Atmospherics**, on directional observations of, 1010.
- Atoms in solutions**, on the magneton numbers of, 375; on partially ionized, 750.
- Ayres** (T. L. R.) on the ionization by collision of hydrogen, nitrogen, and argon, 353.
- Baker** (Dr. H. A.) on the geology of the Falkland Islands, 798.
- Balmer lines**, on generalized quanta and the, 610.
- series of hydrogen, on the distribution of energy in the, 1080.
- Barkla** (Prof. C. G.) on X-ray scattering and on J radiations, 737.
- Beatty** (Dr. R. T.) on the distribution of energy in the Balmer series of hydrogen, 1080.
- Becker** (H. G.) on an apparatus for observing the rate of reaction between gases and liquids, 581.
- Bernoulli's theorem**, on the inversion of, 732.
- Bessel function** $I_n(x)$, tables of the, 846.
- Beta-rays**, on the fluorescence and coloration of glass produced by, 735.
- Bialobjeski** (Prof. Tch.) on the theory of metallic conduction, 161.
- Bickerdike** (C. F.) on the physical interpretation of relativity mathematics, 327; suggestions regarding an alternative theory, 456.
- Bisacre** (F. P. P.) on the skin effect in electrical conductors, 1026.
- Bismuth**, on the photoelectric sensitivity of, 918.
- Boguslawski** (Prof. S.) on the problem of two moving charges, 145.
- Bohr-Sommerfeld orbits**, on the orientation of the, 324.
- Books, new**:—Neville's *Prolegomena to Analytical Geometry in Anisotropic Euclidean Space of Three Dimensions*, 1100; British (Terra Nova) Antarctic Expedition 1910-1913, 1101; *Tables Annuelles Internationales de Constants et Données Numériques de Chimie, de Physique et de Technologie*, 1102; *Kaye's X-Rays*, 1102; *Whitehead's The Principle of Relativity*, with applications to Physical Science, 1103; *Haas & Hill's Introduction to the Chemistry of Plant Products*, 1189; *Eddington's The Mathematical Theory of Relativity*, 1189; *Baker's Principles of Geometry*, 1190; *Thorpe & Ingold's Synthetic colouring Matters: Vat Colours*, 1191.

- Bosanquet (C. H.) on the flow of liquids into capillary tubes, 525.
- Bose (Prof. D. M.) on the ionization tracks of rest atoms, 1050.
- Calcite, on the coefficient of reflexion of X-rays for, 463.
- Capillary curve, on the shape of the, between a plate and a cylinder, 88.
- tubes, on the flow of liquids into, 525.
- Carbon monoxide, on positive rays in, 442.
- Carrington (H.) on the elastic constants of spruce, 1055.
- Castigliano's theorem of least work, on, 193.
- Cathode dis-integration, on, 98.
- fall, on the abnormal, 1149.
- Cathodo-luminescence, on, 957.
- Charges, on the problem of two moving, 145.
- Chaudhuri (K.) on the effect of gases in facilitating the passage of a current, 337.
- Clarke (J. R.) on the fluorescence and coloration of glass produced by beta-rays, 755.
- Colour vision, on the physics of, 1058.
- Coloured flames, on the production of, 336.
- Colours, on the evaluation of the, of the spectrum in terms of the three primary colours, 169.
- Combridge (J. T.) on the gravitational field of a particle on Einstein's theory, 726.
- Compressibility of halogen salts, on the, 882.
- Compton (Prof. A. H.) on the total reflexion of X-rays, 1121.
- Compton (Prof. K. T.) on some properties of resonance radiation and excited atoms, 750.
- Conduction, on the theory of metallic, 161; on, in solutions, 281.
- Conductors, on the skin effect in, 1026.
- Continental displacements, on tidal stresses and, 359, 1167.
- Conway (Prof. A. W.) on the orientation of the Bohr-Sommerfeld orbits, 324.
- Copper, on the photoelectric sensitivity of, 918.
- Core (A. F.) on the meaning of " a " and " b " in the equation of state, 622.
- Cosecants, on the sum of series of, 577.
- Crehore (Dr. A. C.) on the process of light radiation from an atom of a gas, 34.
- Dadourian (Prof. H. M.) on a simple derivation of the Lorentz transformations, 238.
- Davies (Dr. A. C.) on critical electron energies in helium and the extreme ultra-violet spectrum, 786.
- Davis (Prof. B.) on the coefficient of reflexion of X-rays for calcite and rock-salt, 463.
- Delta-radiation, on, 989.
- Deodhar (Prof. G. B.) on the longitudinal elasticity and Poisson's ratio for india-rubber, 471.
- Dispersion, on magnetic rotary, in gases, 560.
- Dissociation-equilibria by the method of partitions, on, 1.
- Dixey (Dr. F.) on the geology of Sierra Leone, 383.
- Dow (E.) on the evaluation of the colours of the spectrum in terms of the three primary colours, 169.
- Drums, on Indian, 315.
- Duffield (Prof. W. G.) on the reaction consequent upon the evaporation of a liquid and upon the emission of vapours from small orifices, 641, 1104; on the mechanism of the electric arc, 1139.
- Earth's surface crust, on the movements of the, 1167.
- Eddington (Prof. A. S.) on the borderland of astronomy and geology, 383.
- Einthoven galvanometer, on temperature measurement with the, 532.
- Elastic constants of spruce, on the, 1055.
- Electric arc, on the mechanism of the, 1139.
- charges, on the problem of two moving, 145.
- conductivity of metals, on the, 161.
- conductors, on the calculation of the skin effect in, 1026.

- Electric fields, on the Stark effect for strong, 1081; on, due to the motion of constant electromagnetic systems, 1191.
- moment of molecules, on the, 849.
- resistance of a hot wire in an alternating air current, on the, 926.
- sparks, on the ignition of gases by, 968.
- Electrolysis with a dropping mercury cathode, on, 303.
- Electrolytes, on the anomaly of strong, 129, 281.
- Electron currents, on the effect of gases in facilitating the passage of, 337.
- energies in helium, on critical, 786.
- Electronic theory of valency, on the, 1105.
- Electrons, on the field of, on Einstein's theory, 276; on the longitudinal and transverse masses of, 760; on the radiation of energy by accelerated, 769; on the emission of secondary, from nickel, 864.
- Elements, on the mass-spectra of chemical, 934.
- Equation of state, on the meaning of "a" and "b" in the, 622.
- Evaporation of a liquid, on the reaction consequent upon the, 641, 1104.
- Ewles (J.) cathodo-luminescence and molecular aggregation, 957.
- Explosion, on the early stages of a submarine, 257.
- Field of an electron on Einstein's theory, on the, 276.
- Flames, on the production of coloured, 336.
- Flint glass of density 6.01, on the electrical properties of a, 516.
- Fluorescence of glass produced by beta-rays, on the, 735.
- Fowler (R. H.) on dissociation-equilibria by the method of partitions, I: on thermodynamics and statistical mechanics, 497.
- Franklin (P.) on tensors of given type in Riemann space, 998.
- Galvanometer, on temperature measurement with the Einthoven, 532.
- Gas-liquid interface, on adsorption at a, 1088.
- Gases, on the process of light radiation from atoms of, 34; on the measurement of the viscosity of, 64; on the molecular scattering of light in, 113; on the effect of, in facilitating the passage of a current, 337; on positive rays in simple, 433; on the radiation and ionization potentials of the rare, 480; on magnetic rotary dispersion in, 560; on an apparatus for observing the rate of reaction between liquids and, 581; on the influence of, on the photoelectric effect with platinum, 593; on the viscosity of, in a transverse electric field, 640; on the ignition of, by electric sparks, 968.
- General Electric Company's Research Staff on cathode disintegration, 98; on the abnormal cathode fall, 1149.
- Geological Society, proceedings of the, 382, 798.
- Geostrophic law, on the temperature of the stratosphere and the, 778.
- Ghosh (R. N.) on inflected waves, 225; on Indian drums, 315.
- Ghosh (S. K.) on the ionization tracks of rest atoms, 1050.
- Gibson (Prof. A. H.) on the impact of hydraulic jets, 229.
- Gill (E. W. B.) on the emission of secondary electrons from nickel, 864.
- Glass, on the electrical properties of a flint, of density 6.01, 516; on the fluorescence and coloration of, by beta-rays, 735.
- Glow discharge, on ionic oscillations in the striated, 879.
- Gravitational deflection of light, on the, 243.
- field of a particle on Einstein's theory, on the, 726.
- Greaves (W. M. H.) on the representative differential equation of the triode oscillator, 401.
- Green (Dr. G.) on the principle of stationary phase in wave-motion problems, 1156.
- Green (H. G.) on the velocity of sound in liquids contained in cylinders with elastic walls, 907.
- Greenhill (Sir G.) on precession of the spinning top, 385, 806.

- Gunnayya (D.) on the emission and absorption of halogens in the visible and ultra-violet regions, 827; on the absorption of potassium vapour, 831.
- Gunningham (S. J.) on the field of an electron on Einstein's theory, 276.
- Halogen salts, on the structure of the, 882.
- Halogens, on the emission and absorption of, 827.
- Havelock (Prof. T. H.) on magnetic rotary dispersion in gases, 560.
- Helium, dimensions of the atom of, 69; on critical electron energies in, 786; on the mass-spectrum of, 935; on ionization by collision in, 1071.
- model, on the spectrum of the semicircular, 1085.
- Heyrovský (Prof. J.) on electrolysis with a dropping mercury cathode, 303.
- Heywood (F.) on the impact of hydraulic jets, 229.
- Hicks (Prof. W. M.) on the radiation and ionization potentials of the rare gases and on the singlet and enhanced series of argon, 480.
- Honda (Prof. K.) on the theory of the specific heat of liquids, 189.
- Hot wire, on the resistance of, in an alternating air current, 926.
- inclinometer, on the, 945.
- Houstoun (Dr. R. A.) on the evaluation of the colours of the spectrum in terms of three primary colours, 169.
- Hydraulic jets, on the impact of, 229.
- Hydrogen, on the temperature ionization of, 19; on light radiation in, 34; on the occlusion of, in palladium, 241; on the ionization by collision of, 353; on the number of radiating atoms in, 430; on positive rays in mixtures of oxygen and, 441; on magnetic rotary dispersion in, 569; on the distribution of energy in the Balmer series of, 1080.
- Hypergeometric functions, on some approximations to, 818.
- Ignition of gases by electric sparks, on the, 968.
- Inclinometer, on the hot-wire, 945.
- India-rubber, on the longitudinal elasticity and Poisson's ratio for, 471.
- Inductances, on the calculation of high-frequency, 783.
- Intramolecular ionization, on, 225.
- Ionic oscillations in the striated glow discharge, on, 879.
- Ionization, on the theory of, by swiftly moving electrified particles, 65; on, by collision, 444; on the, by collision of hydrogen, nitrogen, and argon, 353; on, by collision in helium, 1071; on intramolecular, 1105.
- potentials of the rare gases, on the, 480.
- tracks of rests atoms, on the, 1050.
- Iredale (T.) on adsorption from the gas phase at a liquid-gas interface, 1088.
- Iron, on the mass-spectrum of, 940.
- Isotopes, on the quantum theory and, 801; table of, 244.
- J radiations, on, 737.
- Jeffreys (Dr. H.) on fundamental principles of scientific inquiry, 368.
- Jets, on the impact of hydraulic, 229.
- Joly (Prof. J.) on the movements of the earth's surface crust, 1167.
- Jones (L. T.) on the longitudinal and transverse masses of the electron, 750.
- Jordan (Dr. C.) on the inversion of Bernoulli's theorem, 732.
- Kapitza (P. L.) on the theory of the delta-radiation, 989.
- Kar (Prof. S. C.) on the theory of generalized quanta and the Balmer lines, 610.
- Kunz (Prof. J.) on Planck's law of radiation, 309.
- Lamb (Prof. H.) on the early stages of a submarine explosion, 257.
- Larmor (Sir J.) on the nature and amount of the gravitational deflexion of light, 243.
- Lasareff (Prof. P.) on the number of radiating atoms in hydrogen, 430.
- Least work, on Castigliano's theorem of, 193.
- Lees (S.) on the whirling of an overhung eccentrically loaded shaft, 689.
- Leonard (Dr. A. G. G.) on the aeration of quiescent columns of distilled water and of solutions of sodium chloride, 835.

- Lewis (Prof. G. N.) on physical constants and ultimate rational units, 266.
- Light, on the molecular scattering of, in vapours and gases, 113; in liquids, 213, 625; on the gravitational deflexion of, 243.
- radiation from an atom of a gas, on the process of, 34.
- Lindemann (Prof. F. A.) on the theory of the specific heat of liquids, 1119.
- Liquid-gas interface, on adsorption at a, 1088.
- Liquids, on the reaction consequent upon the evaporation of, 641, 1104; on the specific heat of, 189, 1119; on the molecular scattering of light in, 213, 625; on the flow of, into capillary tubes, 525; on the velocity of sound in, 907.
- Lorentz transformations, on the, 238.
- Lowry (Prof. T. M.) on the electronic theory of valency, 1105.
- Luminescence, on cathodo-, 957.
- Luminous pulsations in the glow of phosphorus, on, 1132.
- McHenry (J. J.) on positive rays in simple gases, 433.
- Magnetic rotary dispersion in gases, on, 560.
- valency and the radiation hypothesis, on, 317.
- Magneton number of an atom in solution, on the, 375.
- Mali (S. M.) on Trouton's law and its applicability at the triple point, 94.
- Mallet (R. A.) on the failure of the reciprocity law in photography, 800.
- Manley (J. J.) on the production of coloured flames, 336.
- Manometer, on an optical, for measurements of viscosity, 84.
- Moss-spectra of chemical elements, on the, 934.
- Mechanics, on thermodynamics and statistical, 497.
- Metallic conduction, on 161.
- Metals, on the spectra of the alkali, 181; on the effect of current on the photoelectric sensitivity of, 918.
- Mercury, on the adsorption of organic vapours by, 1095.
- Mercury cathode, on electrolysis with a dropping, 303.
- Merwe (C. W. van der) on the range of alpha-particles from polonium, 379.
- Molecular aggregation, on cathodoluminescence and, 957.
- scattering of light in gases, on the, 113; in liquids, on the, 213, 625.
- Molecules, on restricted movements of, at low pressures, 414; on the electric moment of, 849.
- Mountain building and the horizontal movements of the earth's crust, on, 1167.
- Morgan (J. D.) on the ignition of gases by electric sparks, 968.
- Narayan (Prof. A. L.) on the emission and absorption of halogens in the visible and ultra-violet regions, 827; on the absorption of potassium vapour, 831.
- Newbould (H. O.) on the Stark effect for strong electric fields, 1081; on the spectrum of the semicircular helium model, 1085.
- Newman (Dr. F. H.) on the relative visibility of spectra when an electric discharge is passed through the vapours of alkali amalgams, 181; on the visibility of individual spectra, 293.
- Nicholson (Dr. J. W.) on the quantum theory and isotopes, 801.
- Nickel, on the emission of secondary electrons from, 864; on the mass-spectrum of, 936.
- Nitrogen, on the ionization by collision of, 353.
- Nitrous and nitric oxides, on the specific heats of, 416.
- Oldham (R. D.) on the earthquake of 7th August, 1895, in Northern Italy, 382; on the Pamir earthquake of 18th February, 1911, 382.
- Optical manometer, on an, for measurement of the viscosity of gases, 84.
- Orbits, on the orientation of the Bohr-Sommerfeld, 324.
- Orifices, on the emission of vapours from small, 641.
- Orr (Prof. W. McF.) on the whirling of an overhung shaft, 708.

- Oscillator, on the differential equation of the triode, 401.
- Oxygen, on positive rays in, 433; on the rate of solution of, by water, 581.
- Palladium, on the occlusion of hydrogen in, 241.
- Partington (Prof. J. R.) on the specific heats of nitrous and nitric oxides, 416.
- Partitions, on dissociation-equilibria by the method of, 1.
- Peddie (Prof. W.) on the physics of colour vision, 1058.
- Peirce (F. T.) on magnetic valency and the radiation hypothesis, 317.
- Phosphorus, on luminous pulsations in the glow of, 1132.
- Photoelectric activity of a potassium ferrocyanide solution, on the variation of the, with concentration, 895.
- experiments on platinum, on, 593.
- sensitivity of metals, on the effect of current on the, 918.
- Photographic emulsion, on the characteristic curve of a, 715.
- exposure, on the quantum theory of, 1062.
- Physical constants and ultimate rational units, on, 266.
- Pidduck (F. B.) on the calculation of high-frequency inductances, 783.
- Platinum, photoelectric experiments on, 593; on the photoelectric sensitivity of, 918.
- Platt (H. H.) on restricted movements of molecules at low pressures, 414.
- Polonium, on the range of alpha-particles from, 379.
- Pomeroy (W. C.) on the longitudinal and transverse masses of the electron, 760.
- Poole (Dr. H. H.) on tidal stresses and continental displacements, 399.
- Poole (Dr. J. H. J.) on the variation of the photoelectric activity of a potassium ferrocyanide solution with concentration, 895.
- Positive rays, on, in simple gases, 433.
- Potassium ferrocyanide solution, on the variation of the photoelectric sensitivity of, with concentration, 895.
- vapour, on the absorption of, 831.
- Precession of the spinning-top, on the, 385, 800.
- Probability of the occurrence of a phenomenon, on the, 732.
- Quanta, or generalized, and the Balmer lines, 610.
- Quantum theory and isotopes, on the, 801.
- — of photographic exposure, on the, 1062.
- Radiation, on Planck's law of, 300; on J, 737; on resonance, 750; on the, of energy by an accelerated electron, 769.
- hypothesis, on magnetic valency and the, 317.
- potentials of the rare gases, on the, 480.
- Raman (Prof. C. V.) on the molecular scattering of light in dense vapours and gases, 113; in liquid mixtures, 213, 625.
- Ramanathan (K. R.) on the molecular scattering of light in dense vapours and gases, 193; in liquid mixtures, 213.
- Rao (K. S.) on the molecular scattering and extinction of light in liquids, 625.
- Reciprocity law, on the failure of the, in photography, 800.
- Relativity, on an alternative theorem in, 456.
- mathematics, on the physical interpretation of, 327.
- Resistance of a hot wire in an alternating air current, on the, 926.
- Resonance radiation, on, 750.
- Richards (R. C.) on the resistance of a hot wire in an alternating air current, 926.
- Richardson (A.) on the aeration of quiescent columns of distilled water and of solutions of sodium chloride, 835.
- Richardson (E. G.) on the theory of the Trevelyan rocker, 976.
- Richardson (Prof. O. W.) on the effect of gases in facilitating the passage of a current, 337.

- Riemann space, on tensors of given types in, 998.
- Rock-salt, on the coefficient of reflexion of X-rays for, 463.
- Rosseland (S.) on the ionization by swiftly moving electrified particles, 65.
- St. Venant, on the principle of, 193.
- Sale (Miss R. R. C.) on X-ray scattering and on J radiations, 737.
- Sand (Dr. H. J. S.) on the anomaly of strong electrolytes, 129, 281.
- Schott (Prof. G. A.) on the radiation of energy by an accelerated electron, 769.
- Scientific inquiry, on the principles of, 368.
- Selenium, on the mass-spectrum of, 941.
- Shaft, on the whirling of an overhung eccentrically loaded, 689.
- Shenstone (A. G.) on the effect of current on the photoelectric sensitivity of metals, 918.
- Shilling (W. G.) on the specific heats of nitrous and nitric oxides, 416.
- Silberstein (Dr. L.) on the quantum theory of photographic exposure, 1062.
- Sirk (H.) on the viscosity of gases in a transverse electric field, 640.
- Skin effect in electrical conductors, on the calculation of the, 1026.
- Smith (J. H.) on the magneton number of an atom in solution, 375.
- Smyth (Dr. J. P.) on the electric moment of the molecule of a substance, 849.
- Sodium chloride, on the aeration of columns of, 835.
- Sound, on the velocity of, in liquids in tubes, 907.
- Southwell (R. V.) on Castigliano's theorem of least work and the principle of St. Venant, 193.
- Specific heats of liquids, on the, 189, 1119; of nitrous and nitric oxides, on the, 416.
- Spectra, on the relative visibility of, 181; on the visibility of individual, 293; on the singlet and enhanced, of argon, 480; on the quantum theory of, 801; on the emission and absorption, of halogens, 827; on the mass, of chemical elements, 934.
- Spectrum, on the evaluation of the colours of the, in terms of the three primary colours, 169; on the ultra-violet, of helium, 786; on the, of the semicircular helium model, 1085.
- Spruce, on the elastic constants of, 1055.
- Stark effect for strong electric fields, on the, 1081.
- Stationary phase, on the principle of the, in wave-motion problems, 1056.
- Statistical mechanics, on thermodynamics and, 497.
- Stellar atmospheres, on the ionization in, 19.
- Stratosphere, on the temperature of the, and the geostrophic law, 778.
- Striated glow discharge, on ionic oscillations in the, 879.
- Submarine explosion, on the early stages of a, 257.
- Surface-tension, on the measurement of, 88.
- Swann (Dr. W. F. G.) on electric fields due to the motion of constant electromagnetic systems, 1911.
- Temperature measurement with the Einthoven galvanometer, on, 532.
- Tensors, on the equality of, 177; on, of given types in Riemann space, 998.
- Terrill (H. M.) on the coefficient of reflexion of X-rays for calcite and rock-salt, 463.
- Thermodynamics and statistical mechanics, on, 417.
- Thomas (Dr. J. S. G.) on the hot-wire inclinometer, 945.
- Thomas (T. Y.) on the equality of tensors, 177.
- Tidal stresses and continental displacements, on, 399, 1167.
- Tin, on the mass-spectrum of, 939.
- Top, on the precession of the spinning, 385, 800.
- Townsend (Prof. J. S.) on ionization by collision, 444, 1071.
- Toy (Dr. F. C.) on the characteristic curve of a photographic emulsion, 715.
- Transformations, on the Lorentz, 238.
- Trevelyan rocker, on the theory of the, 976.

- Triode oscillator, on the differential equation of the, 401.
- Trouton's law, on, 94.
- Tungsten cathode, on the disintegration of a, 98.
- Ultra-violet spectrum, on the, of helium, 789.
- Units, on ultimate rational, 266.
- Valency, on the electronic theory of, 1105.
- Vapour-pressure equation, on the, 29.
- Vapours, on the emission of, from small orifices, 641.
- Viscosity of gases, on the measurement of the, 64; on the, in a transverse electric field, 640.
- Virial equation, on the, 622.
- formula, on Ghosh's and Milner's, 135.
- Wagstaff (J. E. P.) on the application of an optical manometer to the measurement of the viscosity of gases, 84; on the shape of the capillary curve between a flat glass plate and a circular cylinder, 88.
- Waran (Dr. H. P.) on luminous pulsations in the glow of phosphorus, 1132.
- Water, on the rate solution of oxygen by, 581; on the aeration of columns of, 835; on the adsorption of organic vapours by, 1095.
- Watson (Prof. G. N.) on the sum of a series of cosecants, 577.
- Watt (R. A. W.) on directional observations of atmospherics, 1916-1920, 1010.
- Wave-motion problems, on the principle of stationary phase in, 1156.
- Waves, on inflected, 225.
- Wells (E. H.) on temperature measurement with the Einthoven galvanometer, 532.
- Welo (Dr. L. A.) on photoelectric experiments with platinum relating to the influence of gases, 593.
- West (A. G. D.) on ionic oscillations in the striated glow discharge, 879.
- Whipple (F. J. W.) on the disturbance of the uniform temperature of the stratosphere by the vertical displacement associated with horizontal motion governed by the geostrophic law, 778.
- Whirling of an overhung eccentrically loaded shaft, on the, 689, 708.
- Woodward (Miss I.) on the structure of the halogen salts, 882.
- Wrinch (Dr. D.) on fundamental principles of scientific inquiry, 368; on some approximations to hypergeometric functions, 818; on tables of the Bessel function $I_n(x)$, 846.
- Wrinch (H. E. H.) on tables of the Bessel function $I_n(x)$, 846.
- X-ray scattering, on, 737.
- X-rays, on the production of characteristic, 65; on the coefficient of reflexion of, for calcite and rock-salt, 463; on the total reflexion of, 1121.
- Xenon, on the mass-spectrum of, 938.
- Yamada (M.) on the occlusion of hydrogen in palladium, 241.

END OF THE FORTY-FIFTH VOLUME.



32101 013471691

